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CARBON–CARBON BOND FORMATION WITH THE AID OF NICKEL CATALYSTS

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A INTRODUCTION

As early as 1954 Reed[1] discovered a new method for preparing cyclic olefines by reacting butadiene in the presence of the so-called "Reppe catalysts" of the type[2] $L_2Ni(CO)_2$, activated by acetylene Highly active carbonyl-free catalysts can be formed by reducing nickel(II)-acetylacetonate with aluminium alkyls in the presence of mono- and diolefins and sometimes phosphines or phosphites[3] In Fig 1 are summarized those ring syntheses which have been carried out with the aid of zerovalent nickel or nickel-phosphine or -phosphite catalysts The syntheses of the eight-[4], ten-[5] and twelve-membered rings[6] from butadiene or butadiene and ethylene have been intensively investigated In the last four years we have attempted to synthesize as many as possible of the mono- and dimethyl derivatives of *cis*-1,2-divinylcyclobutane[7,8], *cis,cis*-cycloocta-1,5-diene[7,9], *cis,trans*-cyclodeca-1,5-diene and *trans*-deca-1,4,9-triene[7,10], *cis,cis,trans*-4,5-dimethyl-cyclodeca-1,4,7-triene[7,11] and cyclododeca-1,5,9-triene[7,12]. We have also investigated the co-oligomerization of butadiene with methylenecyclopropane[7,10] and

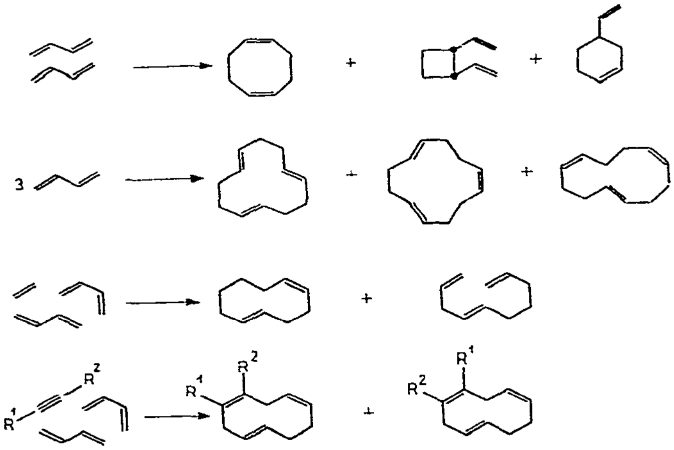


Fig 1 Syntheses of various ring systems promoted by nickel catalysts

allenes[13] In addition, a new catalytic synthesis of 3,4-divinyl-cyclohexenes from 1,3,5-trienes or 1,3,5-trienes and 1,3-dienes has been developed[14,15]. Our principal reason for such a detailed study of these systems, in addition to the preparative synthetic utility, is to obtain an insight into the stereochemistry and mechanism of C—C bond formation We hope that we have found, as a result of our experiments, a new way of looking at the mechanism of C—C coupling with the aid of low-valent nickel catalysts

B SYNTHESES OF MONO- AND DIMETHYL-SUBSTITUTED FOUR-, SIX- AND EIGHT-MEMBERED RINGS

In general a mixture of Ni^0 $(COD)_2$ (ref. 16) and tri(2-biphenylyl)phosphite in a molar ratio 1.1 was used as catalyst[8,14] and the experiments were carried out at 20—40°C. The molar ratio of nickel 1,3-diene, 1,3,5-triene or a 1.1-mixture of 1,3,5-triene and 1,3-diene was 1.50 20% octane was added as an internal standard. The conversion was qualitatively observed by a dilatometer The concentration—time curves of the individual isomers were obtained by gas chromatographic analysis in capillary columns Figure 2 shows from which isomers of piperylene the various four- and eight-membered rings are formed The interpretation of the experimental results[8] starting from piperylene is complicated by two facts first, the equilibria between some four-membered rings and the corresponding 1,3-dienes, and secondly, isomerization of *cis-* into *trans*-piperylene (for experimental details see refs 7, 8, 17) The stereochemistry shown in Fig 2 was easily confirmed by rearranging the pure four-membered rings with a tri(2-biphenylyl)phosphite—nickel catalyst under reduced pressure (50 torr). In this case only the appropriate piperylene isomer is formed and can be removed immediately from the catalyst and the corresponding eight-membered rings

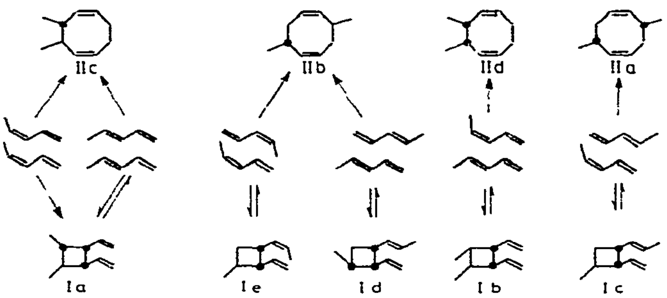
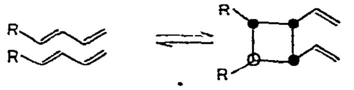


Fig 2 Structures and configurations of four- and eight-membered rings obtained from piperylene with various configurations

The same stereochemistry as observed in the case of *trans*-piperylene is found in the cyclodimerization of *trans*-hexa-1,3-diene[14]. The equilibria between the 1,3-dienes and the four-membered rings depend on the substituents[8,14], e g.



R = H	~3%	~97%
R = CH_3	~80%	~20%
R = C_2H_5	~85%	~15%

The four-membered rings formed are thermally labile compounds[18] and therefore required very mild treatment in the gas chromatographic analysis (the column at 90°C and the inlet system at 100°C) When analyzing the catalytically formed dimers of isoprene, even milder conditions have to be used with the column at 60°C and the inlet system at 90°C Figure 3 shows the products from isoprene using a tri(2-biphenylyl)phosphite–nickel catalyst[14]. In addition, a small percentage of *p*-diprene and dipentene could be identified We isolated the four-membered ring IVa in 16% yield with a 70% conversion of isoprene IVa is thermally extremely labile (half-life at 30°C ~ 30 h) The four-membered rings IVb and IVc are

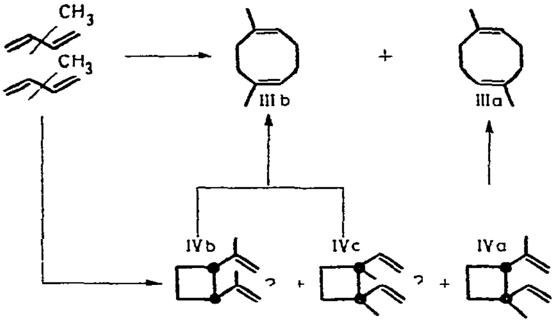


Fig 3 Catalytically formed four- and eight-membered rings from isoprene

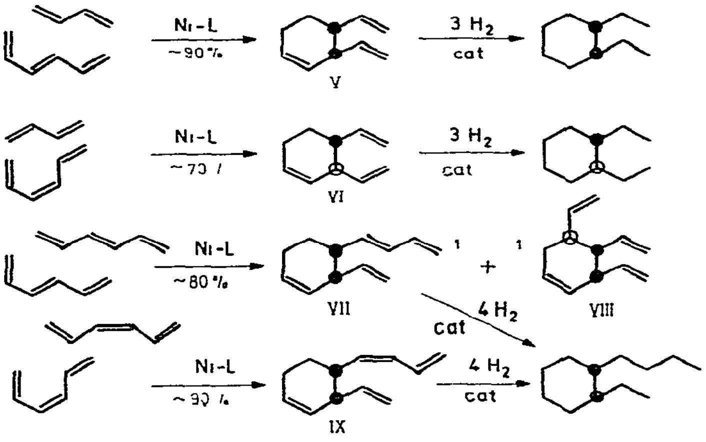


Fig 4 3,4-Divinyl-cyclohexene derivatives from 1,3,5-trienes and 1,3,5-trienes and butadiene Yields based on converted hexa-1,3,5-trienes formed only in less than 1% yield, which may however be due to thermal rearrangement even under the mild reaction and gas chromatographic conditions which we used

Figures 4 and 5 show how individual derivatives of 3,4-divinyl-cyclohexene are formed. In the codimerization of all-*trans*-octa-2,4,6-triene with butadiene the 1,3-diene is bubbled into a solution of the catalyst in the 1,3,5-triene Using tri(2-biphenylyl)phosphite as ligand, practically no four- or eight-membered rings are formed In the other codimerizations shown in Fig 5 we reacted a mixture of the diene and the triene in a molar ratio 1 1. All individual codimers were isolated in pure form by distillation or preparative gas chromatography The experimental details have been described by Wiese[14] and will be published shortly[15]

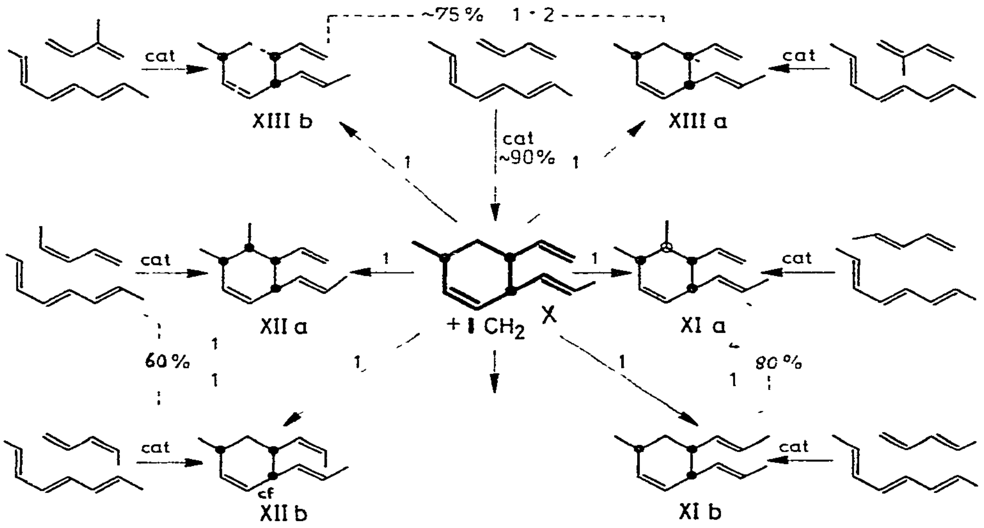


Fig 5 Codimers of all-*trans*-octa-2,4,6-triene and 1,3-dienes In the MIR process the isomers are formed with a statistical weight of one Yields based on converted all-*trans*-octa-2,4,6-triene

C. SYNTHESES OF MONO- AND DIMETHYL-SUBSTITUTED *cis trans*-CYCLODECA-1,5-DIENES AND *trans*-DECA-1,4,9-TRIENES

The catalytic co-oligomerization and cross-co-oligomerization of various 1,3-dienes and olefines allow us to synthesize various mono- and dimethyl derivatives of *cis,trans*-cyclodeca-1,5-diene and *trans*-deca-1,4,9-triene (see Sect D) Thus, we synthesized dimethyl-*cis,trans*-cyclodeca-1,5-dienes from

(1) isoprene and ethylene (94%)
(2) *cis*-piperylene and ethylene (69%)
(3) *trans*-piperylene and ethylene (76%)
(4) a mixture of *cis*- and *trans*-piperylene and ethylene (75%)

In the reaction mixture of butadiene and isobutene or *trans*-butene we could not detect any co-oligomers

We synthesized mono-methyl-*cis,trans*-cyclodeca-1,5-dienes from

(1) butadiene and propylene (8%)

(2) butadiene, isoprene and ethylene (23%)

(3) butadiene, piperylene (*cis*-, *trans*- and *cis, trans* mixtures) and ethylene (21%). In this case butadiene was slowly added to the reaction mixture.

The total yield of cyclic and open-chained co-oligomers of the desired type is given in parentheses as a percentage of the reaction mixture (see Fig 6). In all experiments a triphenylphosphite–nickel catalyst was used The initial ratios of the olefines were

diene ethylene or propylene = 1 1
diene^1 diene^2 ethylene = 1 ·1 1

The reaction temperature was 40°C Further experimental details are described in refs 7 and 10

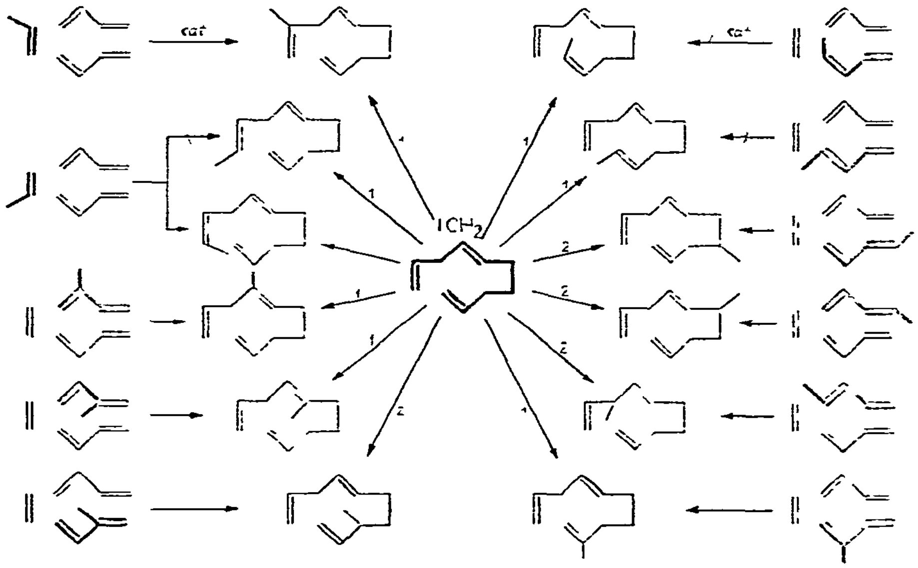


Fig 6 All mono-methyl derivatives of *trans*-deca-1,4,9-triene prepared by MIR In addition, the possible catalytic synthesis is shown

In the co-oligomerization of butadiene with allene (molar ratio = 10 1) up to 70% yield (based on converted allene) of the ten-membered rings may be obtained by keeping the stationary concentration of the allene in the reaction mixture small[12,13] The corresponding ten-membered rings are formed by reacting a mixture of methylenecyclopropane and butadiene.

D PROOF OF THE STRUCTURES

Besides IR and ^{1}H-NMR spectroscopy, two reactions have contributed substantially to the elucidation of the structures and configurations of mono- and dimethyl-substituted *cis*-1,2-divinylcyclobutanes and *cis,trans*-cyclodeca-1,5-dienes The first is the thermal Cope rearrangement of 1,5-dienes (see Fig 7)

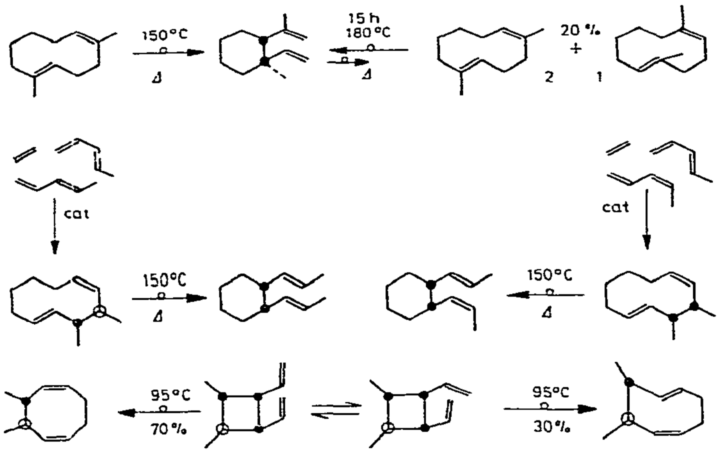


Fig 7 Thermal Cope rearrangements of 1,5-dienes

The second is the methylene-insertion reaction (MIR) (see Figs 5 and 6) The results of these investigations are discussed in detail in ref 7 The stereochemistry of those products, which are of importance in discussing the reaction mechanism, is shown in Figs 5 and 6 One example is sufficient to demonstrate the usefulness of the MIR method, that being the identification of the trimethyl derivatives of *cis*-3,4-divinylcyclohexene[14,15] Diazomethane decays on irradiation into nitrogen and highly reactive methylene Von Doering et al were able to show[19] that the methylene is inserted almost statistically into the C—H bonds of the substrate and Richardson, Dvoretzky and co-workers[20,21] and Schomburg[22,23] succeeded in identifying a great variety of next-higher homologues of saturated and unsaturated hydrocarbons In addition, if double bonds are present in the molecule, cyclopropane derivatives are formed A decisive advantage of the MIR method is that there is no alteration in the configurations and the structures of the attacked molecules The diazomethane is used in 1—3 mole percent of the substrate to avoid the formation of dimethyl derivatives The cocyclodimer X from butadiene and all-*trans*-octa-1,4,6-triene was the key substance in the elucidation of trimethylsubstituted *cis*-3,4-divinyl-cyclohexenes (see Fig. 5). In the MIR mixture of X, all the expected isomers could be separated in two capillary columns of different polarity All six-membered codimers of all-*trans*-octa-2,4,6-triene with *cis*-piperylene, *trans*-piperylene or isoprene had the same retention behaviour as one of the MIR products This means that in all codimers the configuration and structure

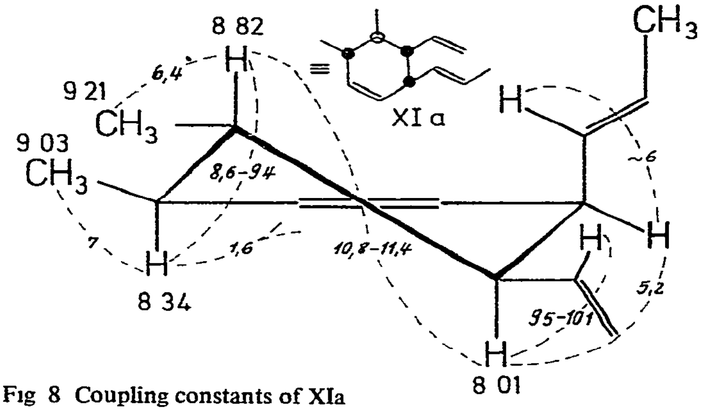


Fig 8 Coupling constants of XIa

of the starting material has been retained. The final identification of the codimers was ascertained by careful ^{1}H-NMR measurements[15] In Fig 8 all τ values and coupling constants for XIa are shown as an example

E DISCUSSION

First we shall outline the mechanism which we favour for carbon–carbon bond formation using a nickel–ligand catalyst[24] and then briefly summarize some of the facts which support this mechanism

We regard the processes which occur at the metal, for example the cycloaddition of 1,3-dienes or 1,3-dienes with an olefin, allene or alkyne, as occurring in a series of intramolecular redox processes, whereby each individual step is a symmetry-controlled process and the individual C–C coupling processes can be regarded as hetero-ring-closure reactions which occur in the sense of the Woodward–Hoffman rules In addition, a C_8-chain formed from two butadiene molecules and attached to the central nickel atom is believed to play a significant role in the four-, six- and ten-membered ring syntheses[25 26]

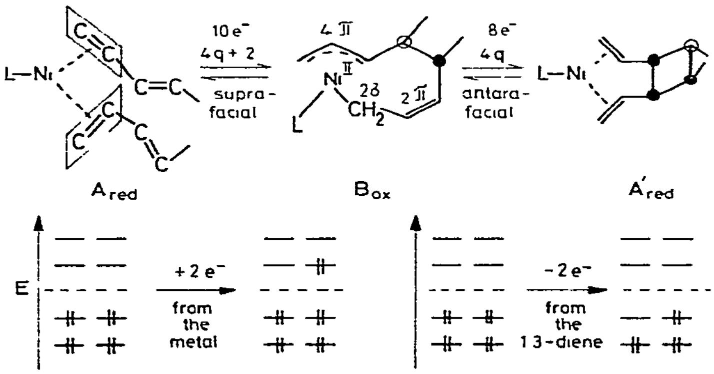


Fig 9 Activation of the 1,3-dienes. (a) by nucleophilic attack of the metal, and (b) by electrophilic attack of the metal

We suggest that the trigonal nickel complex A_{red} rearranges to the square-planar nickel complex B_{ox}, in which process the nickel atom is oxidized from Ni^0 to Ni^{II} with simultaneous reduction of the olefinic ligands (Fig 9) In other words, an alteration in the geometry of the complex A_{red} leads to nucleophilic attack of the metal on the olefinic ligand with simultaneous C–C bond formation The first step – we believe – involves suprafacial C–C bond formation between an *s-cis* and an *s-trans*-1,3-diene A total of ten π-electrons are involved in the rearrangement of the olefinic ligands, eight from the two 1,3-dienes and two from the metal *cis*-1,2-Divinylcyclobutane is formed by antarafacial C–C bond formation with simultaneous reduction of the nickel (A'_{red}) In this process eight electrons of the olefinic system are involved – four from the π-allyl group, two from the uncomplexed *cis* double bond and two σ-electrons from Ni–C bond

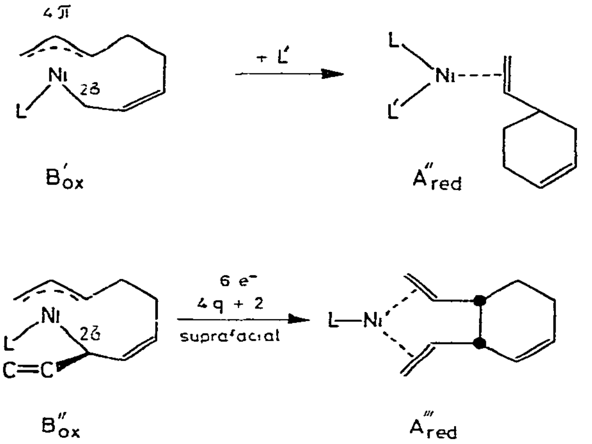


Fig 10 4-Vinylcyclohexene and 3,4-divinylcyclohexene formation by reducing Ni^{II} to Ni^0

Complexation of a further ligand, L', to complex B'_{ox} leads to formation of 4-vinylcyclohexene as a result of suprafacial C–C bond formation (Fig 10) Only six electrons of the olefinic system are involved in this process, four from the π-allyl group and two from the Ni–C bond. The group L' can be an intramolecular ligand, for example a vinyl group, in which case 3,4-divinylcyclohexene is formed and the four-membered ring-synthesis is suppressed

It is our opinion that redox processes and equilibria are of fundamental importance in transition-metal-catalyzed C–H and C–C bond formation and cleavage We will shortly publish in more detail the stereochemical and structural consequences of this electrophilic and nucleophilic attack upon the π-bonded olefinic ligands It is apparent that the relative electron affinity and ionization potential of the π-bonded olefinic groups will control their relative reactivity in reductive or oxidative processes[27]

We assume that the *trans*-deca-1,4,9-trienes and the *cis,trans*-cyclodeca-1,5-dienes are both formed by reaction of the *trans*-π-allyl group of the complex B'_{ox} with a further complexed mono-olefin molecule. This is accompanied by nucleophilic attack of the olefin

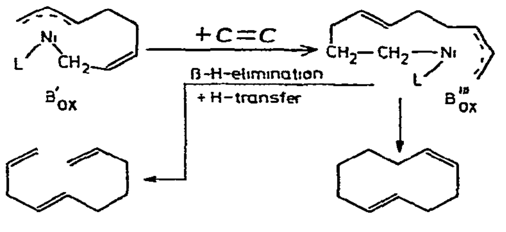
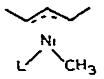


Fig 11 Nucleophilic exchange reaction going from a Ni^{II} to a Ni^{II}-complex

on the metal and at the same time a nucleophilic attack of the *trans*-π-allyl group on the olefin forming the complex B'''_{ox} (Fig 11). Whether open-chain or cyclic C_{10}-derivatives are formed is controlled in part by the electronic character of the ligand L Numerous data are now available which can be elegantly explained by invoking this mechanism which is in addition supported by the reactions of a variety of model nickel(0) and nickel(II) compounds A few examples of these model complexes are shown below (with reference numbers)



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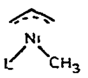

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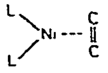

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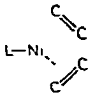

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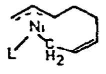

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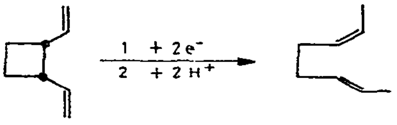
A further example of the process depicted as $A'_{red} \rightarrow B_{ox}$ is provided by the reduction of *cis*-1,2-divinylcyclobutane with sodium in liquid ammonia which, after hydrolysis, leads in high yield to *cis,trans*-octa-2,6-diene — perhaps an example of a reductive-symmetry-controlled ring-opening process[33]



REFERENCES

1 H W B Reed, *J Chem Soc*, (1954) 1931
2 W Reppe and W J Schweckendiek, *Justus Liebigs Ann Chem*, 560 (1948) 104.
3 G Wilke et al, *Angew Chem*, 75 (1963) 10, *Angew Chem, Int Ed Engl*, 2 (1963) 105
4 W Brenner, P Heimbach, H Hey, E W Muller and G Wilke, *Justus Liebigs Ann Chem*, 727 (1969) 161
5 P Heimbach and G Wilke, *Justus Liebigs Ann. Chem*, 727 (1969) 183
6 B Bogdanović, P Heimbach, M Kroner, G Wilke, J Brandt and E G Hoffmann, *Justus Liebigs Ann. Chem*, 727 (1969) 143
7 P Heimbach et al, *Aspects of Homogeneous Catalysis*, Vol 2, in press

8 H Hey, *Thesis*, Ruhr-Universitat, Bochum, 1969

9 P Heimbach, *Mod Chem Ind Proc I U P A C Symp*, *Eastbourne 1968*, p 223

10 H A Buchholz, *Thesis*, Ruhr-Universitat, Bochum, 1971

11 F Thomel, *Thesis*, Ruhr-Universitat, Bochum, 1970

12 H Selbeck, *Thesis*, Ruhr-Universitat, Bochum, 1972

13 P Heimbach, H Selbeck and E Troxler, *Angew Chem* , 83 (1971) 731, *Angew Chem. Int Ed Engl* , 10 (1971) 659

14 W Wiese, *Thesis*, Ruhr-Universitat, Bochum, 1972

15 P Heimbach, J Leitich and W Wiese, unpublished work

16 B Bogdanović, M Kroner and G Wilke, *Justus Liebigs Ann Chem* , 699 (1966) 1

17 P. Heimbach, W Brenner and H Hey, *Vertragsber Symp Koordinationschem Übergangselemente, Jena, 1969*, Sect C, p 62

18 E Vogel, *Justus Liebigs Ann Chem.*, 615 (1958) 1, G S Hammond and C D de Boer, *J Amer Chem Soc* , 86 (1964) 899.

19 W E von Doering, R G Buttery, R G Laughlin and N Chaudhury, *J Amer Chem Soc* , 78 (1956) 3224

20 M C Simmons. D B Richardson and C R Durett, in R P W Scott (Ed), *Gas Chromatography*, 1960, Butterworth, London, 1960, p 211

21 T Dvoretzky, D B Richardson and C R Durett, *Anal. Chem.*, 35 (1963) 545

22 G. Schomburg, *Anal Chim Acta*, 38 (1967) 45

23 G Schomburg, *Chromatographia*, 4 (1971) 286

24 In part discussed by P Heimbach, Bressanone Conf , Bressanone, 1971, and at Leeds–Sheffield Symposium, Leeds, 1971

25 G Wilke, *Pure Appl Chem* , 17 (1968) 179

26 P Heimbach, W Brenner, H Hey and G Wilke, *Proc Int Conf Coord Chem 11th, Haifa 1968*, p 10

27 P Heimbach and H Lehmkuhl, unpublished work

28 H Schenkluhn, *Thesis*, Ruhr-Universitat, Bochum, 1971

29 B Bogdanovic, H Bonnemann and G Wilke, *Angew Chem.*, 78 (1966) 591, *Angew Chem., Int Ed Engl* , 5 (1966) 582

30 G Wilke and G Herrmann, *Angew Chem* , 74 (1962) 693

31 P W Jolly, I Tkatchenko and G Wilke, *Angew Chem* , 83 (1971) 328, *Angew Chem , Int Ed Engl* , 10 (1971) 329

32 P W Jolly, I Tkatchenko and G Wilke, *Angew Chem* , 83 (1971) 329, *Angew Chem , Int Ed Engl* , 10 (1971) 329

33 H Hey, *Angew Chem* , 83 (1971) 144, *Angew Chem , Int Ed Engl* , 10 (1971) 132