Journal of Organometallic Chemistry, 80 (1974) 267—274

NICKEL-CATALYZED REACTION OF BUTADIENE WITH STRAINED RING OLEFINS

FORMATION OF A FOUR-MEMBERED CYCLIC COMPOUND

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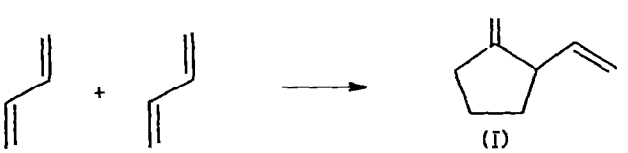
(Received May 2nd, 1974)

Summary

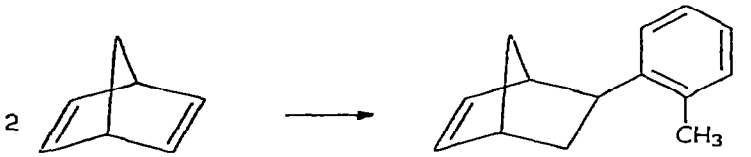
Reaction of butadiene with strained ring olefins such as norbornene, dicyclopentadiene etc. gives an *exo*-methylene- and methyl-substituted four-membered cyclic compound (II). The effective catalysts are $(n\text{-}Bu_3P)_2NiBr_2/NaBH_4$ or /alkoxide (1/1), *syn*-π-crotylbis(triethyl phosphite)nickel hexafluorophosphate (IV), and tetrakis(triethyl phosphite)nickel/CF_3COOH (1/1). π-Crotyl complex IV reacts with the strained ring olefins to give the corresponding product similarly. It is concluded that the active species for this catalytic reaction is a nickel hydride and that this reaction proceeds through a π-crotyl intermediate.

Introduction

The cyclodimerization of butadiene (eqn. 1) to 2-methylenevinylcyclopentane (MVCP, I) induced by some nickel complexes has been reported [1]. In this reaction a ligand-containing zerovalent nickel, combined with some protic acids, has been proven to be an active species. Not only the cyclodimerization of butadiene but also the following reactions of diolefins occur in the presence of such catalysts: (i) *trans*-1,4-polymerization of butadiene [2], (ii) amination of 1,3-diolefins [3] and norbornadiene [4], (iii) allyl transfer [5], and (iv) a novel dimerization of norbornadiene to *exo*-5-(*o*-tolyl)-2-norbornene (eqn. 2) [6]. In the course of a synthetic study using 1,3-diolefins it has been found that butadiene in the presence of such catalysts reacts with strained bicyclic olefins such as dicyclopentadiene, norbornene etc. to afford a four-membered cyclic compound (eqn. 3) [7].



(I) (1)



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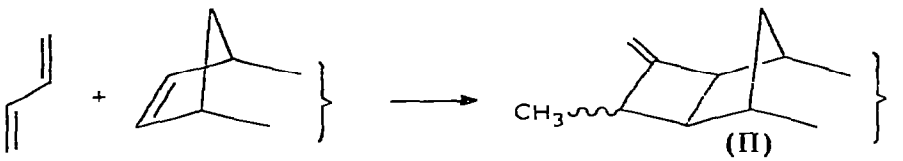


(II)

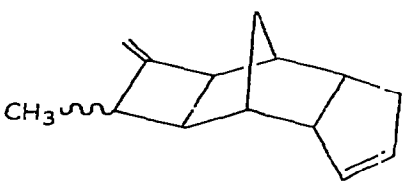
(3)

This catalytic system is different from the conventional ligand-containing zerovalent nickel catalysts developed by Wilke and coworkers [8] in requiring a protic acid. All reactions can be explained in terms of a mechanism involving acid-promoted reactions of nickel(0) complexes.

While the cyclization of a metal-containing unsaturated intermediate to a five-membered cyclic compound is a general and well-characterized reaction in terms of "internal insertion" [9,10], a mechanistic study of the reaction (e.g., eqn. 3) involving hydrogen transfer, is so far lacking. Recently, a few examples of "unusual" cycloadditions of diolefins by palladium [11] and titanium [12] have been reported. This paper is concerned with reaction 3 in detail.

Results and discussion

The reaction of butadiene (BD) with strained bicyclic olefins such as dicyclopentadiene (DCPC) in alcohol in the presence of $(n\text{-}Bu_3P)_2NiBr_2/NaBH_4$ (1/1) affords a 1/1-addition product (BD/DCPD, II) of butadiene and dicyclopentadiene accompanied by a small amount of I. The product II gave mass, NMR and infrared spectral data consistent with the assigned structure. Its in-



(BD/DCPD, II)

frared spectrum shows a strong absorption at 880 cm^{-1} due to the terminal methylene group. The NMR spectrum of II (Fig. 1, A) (BD/DCPD) has absorptions due to olefinic protons at δ 5.4 and 4.7 and a sharp doublet (J = 7 cps) at δ 1.1 due to the methyl protons. The two absorptions at δ 4.7 and 1.1 are completely absent in the NMR spectrum of II (BD-d_6/DCPD) (Fig. 1, B) which was obtained from the reaction of hexadeuteriobutadiene (BD-d_6) with DCPD. The infrared spectrum of II (BD-d_6/DCPD) no longer has absorptions at 880 cm^{-1} due to the $=CH_2$ group and at 1370 cm^{-1} due to the methyl group. The stereochemistry at the methyl-bearing carbon atom has not been established. Because the NMR spectrum is too complicated to use decoupling techniques, the *exo*- or *endo*-configuration of the cyclobutane ring with respect to the methylene bridge

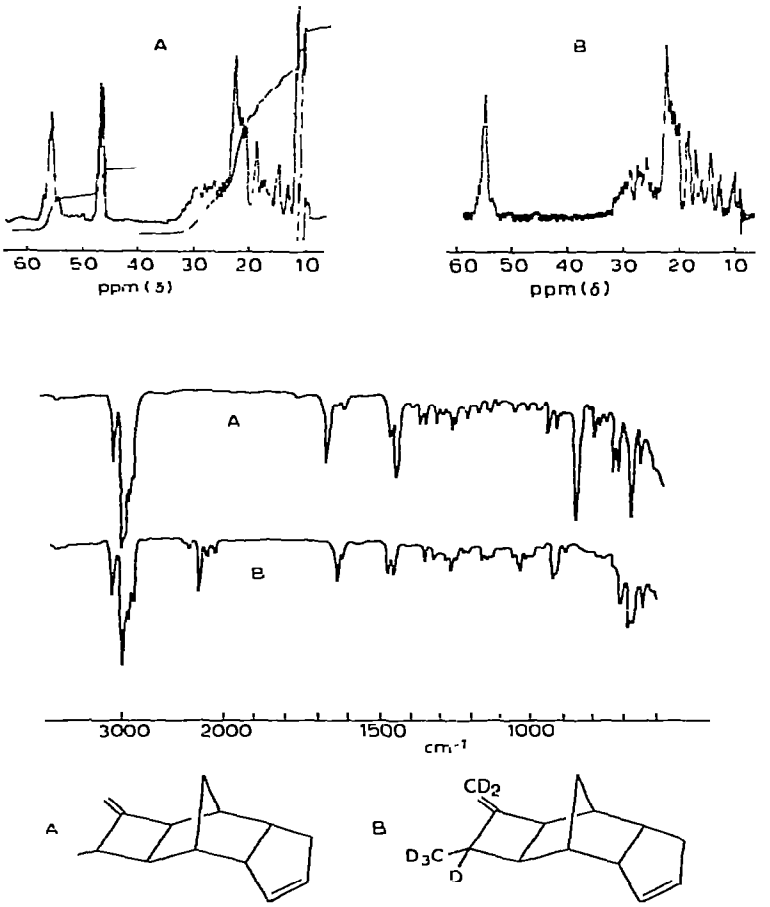


Fig. 1 NMR and IR spectra of II. A, BD/DCPD, B, BD-d_6/DCPD.

has not yet been conclusively identified. However, the ring is tentatively thought to be in the *exo*-configuration for the reasons described below.

Tertiary phosphine complexes of nickel bromide with sodium borohydride were the most effective catalysts. The systems $NiBr_2$(pyridine)$_2$/$NaBH_4$, $NiBr_2$/$NaBH_4$, or (n-$Bu_3P)_2NiBr_2$ by themselves were ineffective. Sodium alkoxide can also be used in place of $NaBH_4$ for the reducing agent. The ratio of RO^-/Ni or $NaBH_4$/Ni has a great influence on the distribution of the products (Table 1). Use of an equimolar amount of alkoxide and the nickel compound is effective for the formation of II and I. The catalytic system of this composition gives a phosphine-containing zerovalent nickel and hydrogen bromide under the reaction conditions, as proposed in the previous paper [1]. Addition of more alkoxide gives, on the other hand, a conventional zerovalent nickel complex, which affords only isomeric n-octatrienes [8]. The catalytic efficiencies of different nickel complexes are shown in Table 2. This reaction can be applied to other strained ring olefins. The reaction of butadiene with norbornene and 5-ethylidene-2-norbornene affords the corresponding products in moderate yields. The products of butadiene with other olefins also have the strong absorption at 880 cm^{-1}

TABLE 1

EFFECT OF ALKOXIDE AS REDUCING AGENT AT 80°C[a]

Alkoxide (mM)		Solvent (ml)		Yield (%)		
				MVCP	OT[b]	$C_{14}H_{18}$ (II)
EtONa	(1)	EtOH	(3)	58	0	19
EtONa	(2)	EtOH	(3)	0	90	0
EtONa	(5)	EtOH	(3)	0	90	0
t-BuONa	(1)	t-BuOH	(3)	0	0	63

[a] $NiBr_2(n\text{-}Bu_3P)_2$, 1 mM. [b] Octatrienes.

due to the terminal methylene group. Inspection of Tables 1 and 2 reveals that the cyclodimerization of butadiene to I and the cycloaddition occur competitively

It has previously been reported that the active species for the cyclodimerization (eqn. 1) is formed from some ligand-containing zerovalent nickel complexes and protic acid. The reaction of the Ni^0 complexes with protic acid attains the following equilibrium*:

$$HX + NiL_4 \rightleftarrows \underset{(III)}{HNiL_4^+ X^-} \qquad (4)$$

which lies far to the left but is still effective for the cyclodimerization. It is well-known that the reaction of a nickel hydride with a 1,3-diolefin affords a π-allyl complex [14]. Consequently, if the nickel hydride, which is formed from the above equilibrium, is an active species for this cycloaddition (eqn. 3) to II, a π-allyl nickel complex might be a key intermediate of this reaction. Therefore, we investigated the use of a π-crotylnickel complex to gain insight into the reaction. *syn*-π-Crotylbis(triethyl phosphite)nickel hexafluorophosphate (IV)

TABLE 2

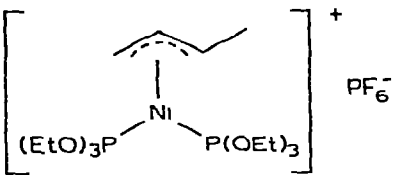
REACTION OF BUTADIENE WITH DICYCLOPENTADIENE[a]

Nickel compound	Yield[b] (%)	
	MVCP	$C_{14}H_{18}$ (II)
$NiBr_2(n\text{-}Bu_3P)_2$	10.1	73
$NiCl_2(n\text{-}Bu_3P)_2$	24.2	15
$Ni(NO_3)_2(n\text{-}Bu_3P)_2$	6.6	trace
$Ni(SCN)_2(n\text{-}Bu_3P)_2$	22.5	10.3
$NiBr_2(Ph_3P)_2$	11.0	51

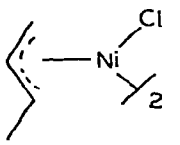
[a] [Ni] = [$NaBH_4$] = 1.5 mM; [BD] = 36 mM; [DCPD] = 20 mM; EtOH, 4 ml, all reactions were carried out at 80°C for 20—24 h. [b] MVCP on butadiene used and II on DCPD.

* For example, the catalytic system of $Ni[P(OEt)_3]_4/CF_3COOH$ is favorable for the formation of I [2b]. The equilibrium constant for reaction 4 (L = $P(OEt)_3$, $X^- = CF_3COO^-$) in $CDCl_3$ is approximately 0.3. [13].

[14] was prepared for this purpose.

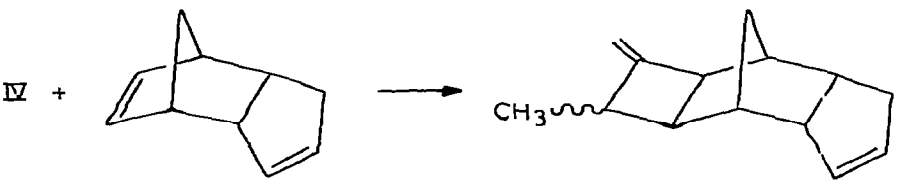


(IV)



(V)

The π-crotyl complex IV was allowed to react with DCPD in ethanol at 80°C. The product II was obtained in ca. 60% yield. Similarly, π-crotyl complex V gave II in low yield in the presence of 2 equivalents of tri-n-butylphosphine.



(5)

(II)

It has also been found that reaction 3 proceeds smoothly in the presence of a catalytic amount of IV without added acid. On the other hand, when tetrakis(triethyl phosphite)nickel, $Ni[P(OEt)_3]_4$, is used as the catalyst, addition of a controlled amount of protic acid such as trifluoroacetic acid is necessary.

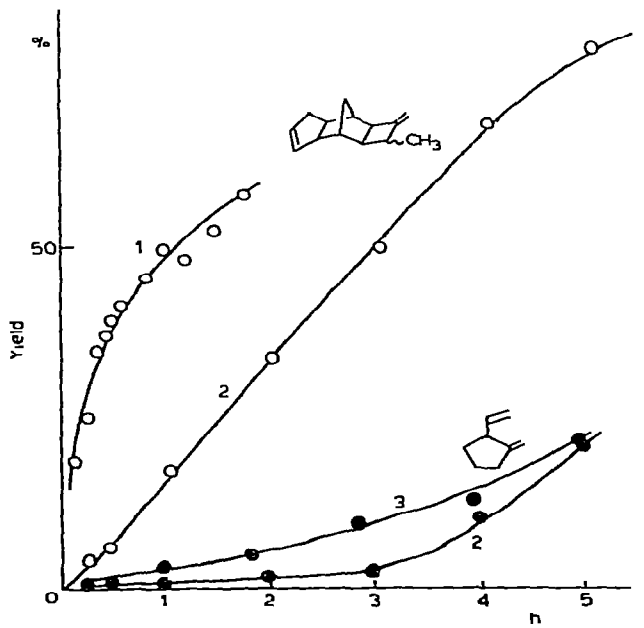
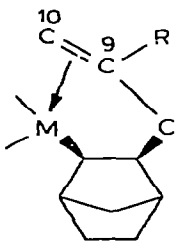


Fig. 2. Rates of reaction of $[\pi\text{-}C_4H_7NiL_2]^+PF_6^-$ with DCPD (1), of butadiene with DCPD by $(n\text{-}Bu_3P)_2NiBr_2/NaBH_4$ (1/1) (2), and of butadiene by $(n\text{-}Bu_3P)_2NiBr_2/NaBH_4$ (1/1) (3). Conditions: in ethanol at 80°C.

To gain more detailed insight into the reaction, the rate of the formation of II was investigated. The reaction of IV with DCPD (eqn. 5) in ethanol at 80°C is shown in Fig. 2 (curve 1). The yellow complex (IV) gradually turned deep-red. After 15 min a considerable amount of II was formed (19% yield) and a high yield (>60%) was realized within 2 h. In the catalytic reaction (eqn 3), I and II are formed competitively. 2-Methylenevinylcyclopentane (I) is formed with a Ni^0—acid system. A larger amount of II (than I) is formed with a H—Ni catalyst, although the equilibrium expressed by eqn. 4 is considered to lie far to the left under the reaction conditions [13]. Consequently, it is interesting to compare the rates of formation of these two compounds. An experiment was carried out using $(n\text{-}Bu_3P)_2NiBr_2/NaBH_4$ (1/1) system as the catalyst. In this case the formation of II is more rapid than that of I (see Fig. 2, curves 2). The latter is formed only after a considerable amount of DCPD is consumed. The formation of I is so sufficiently slow even in the absence of DCPD (curve 3) [15] that the formation of II is possible with a small amount of the active H—Ni species.

Recently, insertion of bicyclic olefin into nickel— or palladium—allyl bonds has been reported [16] and *cis-exo* addition of the metal—carbon bond to the double bond has been established by X-ray structural analysis and the deuterium-labelling experiments (see VI) [17,18]. From these results the stereochemistry of the four-membered cycle in II was tentatively concluded to be of the *exo*-configuration described above.



(VI a) M = Pd
(VI b) M = Ni

(VI)

We attempted the reaction of π-crotylpalladium chloride with norbornene in boiling benzene. However, no isolable cyclic organic compound was detected by gas chromatography even when the solution was heated in the presence of tri-n-butylphosphine or under an atmosphere of carbon monoxide. Although the structure of the insertion product of the square planar palladium complex (VIa) has been well-characterized, structural data of the isolable analog of nickel complex (VIb) appear to be scarce [16a]. In connection with the reaction mechanism, however, X-ray structural studies on the palladium complex (VIa) will shed light on the explanation of the nickel-catalyzed cyclization to II. The C(9)—C(10) bond axis is tilted in towards the palladium. The angle, which depends on the strain in the carbon chain, seems to vary to a certain extent with the nature of the anionic ligand [16,17]. Although from the present study the detailed mechanism of this reaction is obscure, the strain in the carbon chain is one of the explanation for this "unusual" stepwise cycloaddition giving the four-membered cyclic compound.

Experimental

Tetrakis(triethyl phosphite)nickel [19], *syn*-π-crotylbis(triethyl phosphite)-nickel hexafluorophosphate [14], and π-crotylnickel chloride were prepared by known methods. Hexadeuteriobutadiene (isotopic purity > 98%) was prepared from hexachlorobutadiene by the reported method [20]. Commercially available dicyclopentadiene was used without further purification. Analyses and separation of the products were performed by gas chromatography on a 3 m column of Silicon DC 550 on Celite 545 at 200°C. The yields were determined by using tetralin as an internal standard.

Reactions

All reactions were carried out in sealed glass tubes similar to the dimerization of butadiene reported previously [1].

A. Catalytic reactions

In a glass tube (8 or 20 mm in diameter) the nickel complex, sodium borohydride, solvent, dicylopentadiene (or norbornene etc.) and liquified butadiene at −78°C were added in this order under an atmosphere of argon. The tube was sealed and heated without agitation. The reaction conditions were described in Figures and Tables. Gas chromatographic analyses were carried out without separation of the catalyst (retention time: tetralin, 1.9 min; II, 3.8 min).

B. Reaction of π-crotylnickel (IV) with DCPD

In a three-necked flask equipped with a three-way stopcock and a reflux condenser, 1.2 mmol of complex IV, 3 ml of ethanol, 1 ml of dicyclopentadiene, and 0.1 ml of tetralin (an internal standard) were placed under an atmosphere of argon. The flask was heated at 80°C and the reaction mixture was sampled by a micro syringe under an argon atmosphere at various time and analyzed by gas chromatography. The results are shown in Fig. 2.

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