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NICKEL-CATALYZED AMINATION OF 1,3-DIENES

EVIDENCE FOR A π-ALLYL INTERMEDIATE

JITSUO KIJI, EIICHI SASAKAWA, KAZUYOSHI YAMAMOTO and JUNJI FURUKAWA
Department of Synthetic Chemistry, Kyoto University, Kyoto 606 (Japan)
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Summary

syn-π-Crotylbis(triethyl phosphite)nickel hexafluorophosphate reacts with morpholine to give 1-(*N*-morpholino)-2-butene. This π-crotylnickel complex, without added acid, catalyzes the reaction of butadiene with morpholine. From these observations, π-allyl intermediates are proposed as intermediates in the amination of 1,3-dienes. *trans*-1,3-Pentadiene reacts with amines more easily than the *cis*-isomer. The different reactivities are discussed on the basis of the stabilities of π-allyl complexes which are assumed to be key intermediates.

Introduction

Soluble nickel complexes have been shown to be versatile catalysts for many reactions of dienes such as polymerization, oligomerization, and addition of active hydrogen compounds. In the course of the study of the cyclodimerization of butadiene to 2-methylenevinylcyclopentane in secondary amines, it was found that amination and the cyclodimerization of butadiene occur competitively [1]. Recently, several effective transition metal catalysts for the reaction of 1,3-dienes with amines were developed [1—6]. It has been shown that a catalytic amount of a protic acid has a great influence on the amination of 1,3-dienes catalyzed by Ni^0 complexes. A part of this study has been reported in preliminary paper [7]. The present paper is an extension of this study to observe the effect of acidity of the catalytic system and to identify an intermediate in the amination. Tetrakis(triethyl phosphite)nickel, $Ni[P(OEt)_3]_4$, is one of the most easily available zerovalent species and its reaction with acids has been studied extensively by Tolman [8]. Most of the present study employed $Ni[P(OEt)_3]_4$ and its derivatives.

Results and discussion

In this reaction secondary cyclic amines gave the best results. Therefore, morpholine was used exclusively. Nickel catalysts give a mixture of butenyl- and octadienyl-amines by incorporation of one and two units of butadiene, respectively. In this type of amination catalyzed by Ni^0 complexes a catalytic amount of a protic acid such as trifluoroacetic acid or sulfuric acid is necessary as the cocatalyst [7]. Without the acid the reaction of butadiene is very slow and linear dimers are formed in low yield. The reaction of NiL_4 (L = phosphite) with a protic acid in methanol [8], chloroform, benzene, or acetone [9] affords a nickel hydride according to eqn. 1.

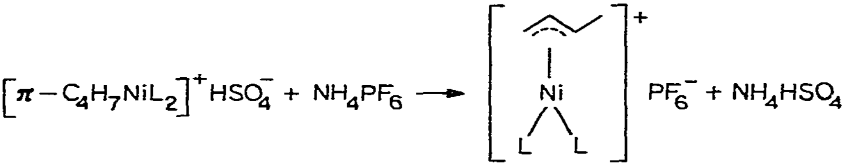
$$HX + NiL_4 \rightleftharpoons [HNiL_4]^+X^- \qquad (1)$$

An attempt was made to detect the active species formed from $Ni[P(OEt)_3]_4$ and trifluoroacetic acid in an amine solvent. A freshly prepared colorless solution of diethylamine, containing $Ni[P(OEt)_3]_4$ and an excess of trifluoroacetic acid ($CF_3COOH/Ni \gtrsim 100$), gradually turns light yellow and shows a weak absorption around 330 nm at room temperature. If the amount of trifluoroacetic acid is small, any absorption at longer wave length than 300 nm is not observed. The absorption at 325 nm of the corresponding methanol solution has been assigned to a characteristic band due to the $[HNiL_4]^+$ species [8]. Thus, it is apparent that a large amount of the added acid is forming the nickel hydride.

It is well-known that the reaction of the nickel hydride species with 1,3-dienes results in the formation of π-allyl complexes [10]. Consequently, the formation of the butenyl amine is likely explained by the attack of an amino group on the carbon atom of a π-crotyl complex formed by the reaction of butadiene with the nickel hydride. To establish this point, the π-crotylnickel complex (I) was prepared by the following reaction according to the method reported by Tolman [11] and allowed to react with morpholine.

$$NiL_4 + H_2SO_4 \rightleftharpoons [HNiL_4]^+HSO_4^- \qquad (2)$$

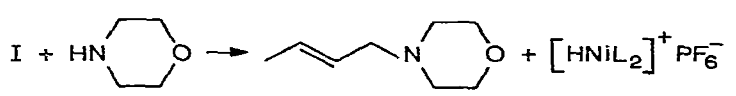
$$[HNiL_4]^+HSO_4^- + C_4H_6 \xrightarrow{2L} [\pi\text{-}C_4H_7NiL_2]^+HSO_4^- \qquad (3)$$



(I)

(4)

The π-crotylcomplex (I) was found (NMR) to be completely in the *syn* form. When 2 mmol of I was heated in 2 ml of morpholine in a sealed tube at 80°, 1-(*N*-morpholino)-2-butene was formed in 35% yield after 15 h. The double bond of the butenyl amine has the *trans* configuration. It is proposed that the nickel hydride complex is the active species in the formation of the butenyl amine from butadiene and the π-crotylcomplex (I) is a key intermediate in the amination of butadiene.


(5)

When this π-crotyl complex was used as the catalyst, a protic acid no longer was necessary to catalyze the reaction of butadiene with morpholine, and the butenyl and octadienyl amines were obtained in moderate yields. In this case the nickel hydride is presumed to be produced as shown in eqn. 5. However, addition of a small amount of trifluoroacetic acid promotes the formation of the butenyl amines as shown in Table 1. This observation is consistent with the previous results [7].

In connection with the mechanism of this amination through the π-allyl intermediate, experiments using *cis*- and *trans*-1,3-pentadiene were very instructive. The amination was carried out with $Ni[P(OEt)_3]_4$ and trifluoroacetic acid (Ni/CF_3COOH 1/10). The *trans* isomer gave 4-(*N*-morpholino)-*trans*-2-pentene (II) (see eqn. 6), while the *cis* isomer gave a mixture of II and 1-(*N*-morpholino)-*trans*-2-pentene (III) (see eqn. 7). The *trans* configuration of the double bonds in II and III was established by the fact that their infrared spectra have a strong absorption at 970 cm^{-1} and no absorption between 670 and 730 cm^{-1}. The time—conversion curves are shown in Fig. 1. An induction period is observed in this amination. During the induction period the solution is colorless. When the solution turns light yellow, the amination begins to occur and finally the solution becomes yellow-orange. The induction period is presumably attributed to the formation of the π-allyl intermediates, since a dissociation of one molecule of the phosphite ligands is required prior to its formation and this dissociation is slow [11]. In fact, in both cases of the reaction of complex I with morpholine and of amination with the $(n\text{-}Bu_3P)_2NiBr_2$—$NaBH_4$ system, no induction period is observed. After the induction period the difference of the reactivities of the isomers is apparent from Fig. 1. In the case of the *trans* isomer a high yield is realized within several hours, while the reaction of the *cis* isomer proceeds very slowly and a large amount of *cis*-1,3-pentadiene is recovered unchanged. Neither an appreciable side-reaction to consume the pentadiene nor isomerization occurs under the reaction conditions.

TABLE 1

AMINATION OF BUTADIENE BY *syn*-π-$C_4H_7Ni[P(OEt)_3]_2 \cdot PF_6$

Conditions: $[Ni] = 0.5$ m*M*, $[C_4H_6] = 10$ m*M*, morpholine = 1 ml, at 80° for 20 h.

CF$_3$COOH/Ni (mol ratio)	Yield (%)	
	$H(C_4H_6)N\!<$ [a]	$H(C_4H_6)_2N\!<$ [b]
0	26	42
0.5	63	5
1.0	69	2
2.0	76	$\ll 1$
3.0	77	—

[a] A mixture of 1-(*N*-morpholino)-2-butene and 3-(*N*-morpholino)-1-butene. [b] A mixture of 1-(*N*-morpholino)-2,7-octadiene and 3-(*N*-morpholino)-1,7-octadiene.

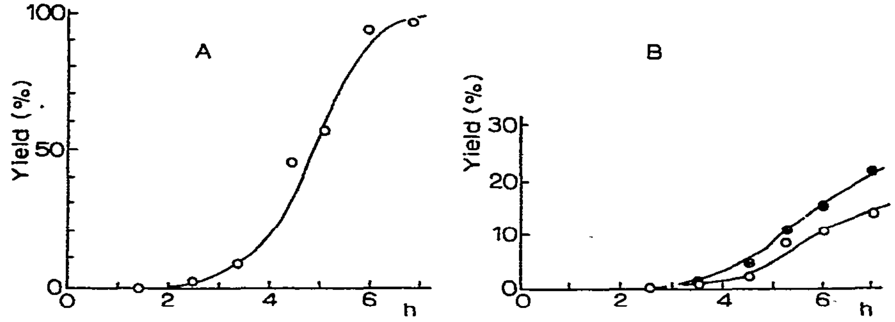
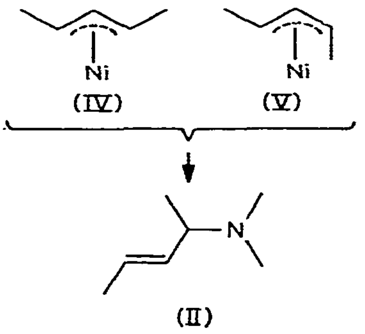
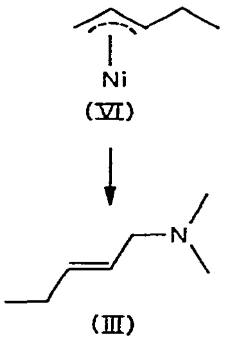


Fig. 1. Rate of reaction of *trans*- (A) and *cis*-1,3-pentadiene (B) with morpholine at 80°; 0.125 × 10^{-3} *M* $Ni[P(OEt)_3]_4$, 1.25 × 10^{-3}*M* CF_3COOH, 0.5 ml C_5H_8, 0.7 ml morpholine. (o) 4-(*N*-Morpholino)-*trans*-2-pentene, (●) 1-(*N*-morpholino)-*trans*-2-pentene.

It is noteworthy that the yield of 4-(*N*-morpholino)-*trans*-2-pentene (II) is much decreased in the case of the *cis* isomer, and 1-(*N*-morpholino)-*trans*-2-pentene (III) is the major product. This fact is explicable in terms of the stability of the π-allyl intermediates. The stable, *syn,syn*-π-dimethylallyl complex (IV) is formed more easily from the *trans* isomer than from the *cis* isomer; a cisoidal coordination is required in this case. For this reason the dimethylallyl complex (IV or V) from the *cis* isomer is formed with such difficulty that an ethylallyl complex (VI) is formed slowly and competitively. The products II and III are formed from IV (or V) and VI, respectively. This explanation is visualized in eqn. 6 and eqn. 7.



(6)



(7)

In fact, when the *trans* isomer of high isomeric purity (>98%) was used, the formation of III was negligibly small. The explanation that III is formed from IV or V is consistent with the results of Tolman; an ethylallyl complex is not formed from the reaction of *trans*-1,3-pentadiene with the nickel hydride [10]. Attempt to detect the formation of ethylallyl complex from the *cis* isomer by NMR spectroscopy was not successful, because its amount is presumed to be very small.

Experimental

The following were synthesized by known methods; tetrakis(triethyl phosphite)nickel [12] and *syn*-π-crotylbis(triethyl phosphite)nickel hexafluorophosphate (I) [11]. Commercially available *cis*- and *trans*-1,3-pentadiene (purities: *cis*, >99%; *trans*, >98%) were used without further purification. Gas chromatographic analyses were carried out on Silicone DC 550 on 3m Celite 545 column. The yields were detetmined using tetralin as an internal standard.

Reactions

All reactions were carried out in sealed glass tubes. The nickel complex was placed in a glass tube (8 mm in diameter). The tube was immediately fitted with a three-way stopcock, through which solvent and reagent were introduced by a syringe. The system was placed under argon by evacuating and filling it with argon several times. Amine, trifluoroacetic acid, and 1,3-diene were added in this order. The tube was sealed with a flame and heated without agitation.

Amination of butadiene with I and CF_3COOH

The following procedure is representative. The complex (I) (0.5 mmol), 1 ml of morpholine, 1 mmol of CF_3COOH (variable as shown in Table 1), and 1 ml of liquified butadiene were heated at 80° for 20 h. Gas chromatographic analysis (150° hydrogen flow at 1 kg/cm^2) showed the presence of three compounds (retention times 1 min; 1 min, 27 sec; and 1 min, 54 sec) in the ratio about 1/3/1. The compounds were shown to be 2-methylenevinylcyclopentane, 3-(*N*-morpholino)-1-butene, *trans*-1-(*N*-morpholino)-2-butene, respectively, by the following spectral data obtained from GC collected samples. 1-(*N*-Morpholino)-*trans*-2-butene, NMR: Multiplets at τ 8.6 (3H), 7.6 (4H of morpholino), 7.2 (2H), 6.5 (4H of morpholine), and 4.5 (2H); IR: A strong absorption at 970 cm^{-1} due to a *trans* —CH=CH— group. 3-(*N*-Morpholino)-1-butene, NMR: A doublet at τ 8.8 (3H, *J* 10 cps), multiplets at 7.6 and 6.5 due to morpholine and a multiplet between 3.9 and 5.1 (2H), and a quintet at 7.0 (1H); IR: 920 and 1000 cm^{-1} due to a terminal vinyl group.

Amination of 1,3-pentadiene with $Ni[P(OEt)_3]_4$ and CF_3COOH

The following procedure is representative for the reaction of *cis*- and *trans*-1,3-pentadiene as shown in Fig. 1. Nickel complex $Ni[P(OEt)_3]_4$ (0.125 mmol), 1.25 mmol of CF_3COOH, 0.7 ml of morpholine, and 0.5 ml of *cis*-1,3-pentadiene were heated at 80° for 4.5 h (variable as shown in Fig. 1). Gas chromatographic analysis (150°, hydrogen flow at 1 kg/cm^2) showed the presence of two compounds (retention times 3 min, 5 sec; and 3 min, 30 sec in the ratio about 1/1.5). The compounds were shown to be II and III, by the following spectral data. 4-(*N*-Morpholino)-*trans*-2-pentene (II), NMR: Two doublets at τ 8.9 (*J* 10 cps, 3H) and 8.3 (*J* 6.7, 3H) and four multiplets centered at 7.7 (4H), 7.2 (1H), 6.5 (4H), and 4.7 (2H); IR: 970 cm^{-1} (*trans* —CH=CH—). 1-(*N*-Morpholino)-*trans*-2-pentene (III), NMR: A triplet at τ 9.0 (*J* 10 cps, 3H), four multiplets centered at 8.2 (2H), 7.7 (4H), 6.5 (4H), and 4.5 (2H), and a doublet 6.2 (*J* 10 cps, 2H). IR: 970 cm^{-1} (*trans* —CH=CH—).

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