

Ni(ethylhexanoate)₂/nligand/Et₂AlCl catalyzed cycloisomerization of 1,6-heptadienes to cyclopentane derivatives

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Abstract

A series of Ni(OEtHex)₂/phosphine/Et₂AlCl systems were used as cycloisomerization catalysts of various 1,6-heptadienes. The best results were obtained with the catalytic system using triphenylphosphine as a ligand. The cycloisomerization with this system afforded the corresponding methyl(methylene)cyclopentane derivatives with high selectivity (40–99%) and in good overall yields of the cyclopentane derivatives (90–96%). The cycloisomerization proceeded also with other derivatives possessing 1,6-diene moiety giving the corresponding methyl(alkenyl)cyclopentane derivatives in good yields (33–90%).

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1. Introduction

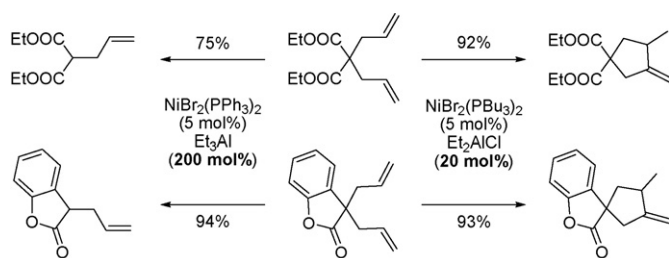
Unactivated alkenes have been considered as a latent functional group compatible not only with traditional methods of C–C bond-forming reactions that use nucleophilic and electrophilic reagents, but also with reactions based on the use of transition metal reagents. The application of transition metal compounds is especially attractive, because it bears attributes relevant to synthetic efficiency: (i) potential for development of catalytic processes and (ii) ligand modification for control of product regio- and stereoselectivity. One of such sought after processes are the transformations of α , ω -dienes to carbo- and heterocycles, because these are widespread structural motifs in biologically active compounds. The development of efficient, stereoselective, and simple methods for the synthesis of these frameworks is of continuing interest in catalysis research. An elegant and atom economic approach [1] to five- and six-membered heterocycles offers the cycloisomerization of 1,6-

dienes [2]. Over the years a number of catalysts based on elements from the beginning or the end of transition metal row have been used to affect this process under various reaction conditions (various reaction mechanisms) and are associated with the names of Negishi and Takahashi (Zr), Waymouth (Zr), Livinghouse (Ti), Itoh (Ru), Grigg (Rh), RajanBabu and Widenhoefer (Pd), Leitner (Ni) and others. As typical examples may serve catalytic procedures using compounds of Zr [3,4], Ti [5], Ru [6–10], Rh [11,12], Ni [13–16], and Pd [11,12a,b,14,17–20].

Recently, we have reported that a simple catalytic system based on a combination of Ni(II)–phosphine complexes and organoaluminums can be used either for the C–C bond cleavage [21] or the C–C bond formation [22] depending on the Ni/organoaluminum ratio. Thus the use of 200 mol% of organoaluminum and 5 mol% of Ni-complex (Ni/Al = 1/40) with the respect to the substrate allowed smooth deallylation, whereas 20 mol% of organoaluminum and 5 mol% of Ni-complex (Ni/Al = 1/4) resulted in the selective cycloisomerization to cyclopentane derivatives. Representative examples are given in Scheme 1. As for the reaction mechanism, likely scenario is outlined in Scheme 2. It is assumed that it involves the formation of a nickel-hydride, followed by hydronickelation of one of the double bonds, intramolecular carbonickelation of the remaining double bond, and β -hydrogen elimination. In the last

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Scheme 1. The C–C bond cleavage and formation reactions of 1,6-dienes in the presence of Ni/R₃Al systems.

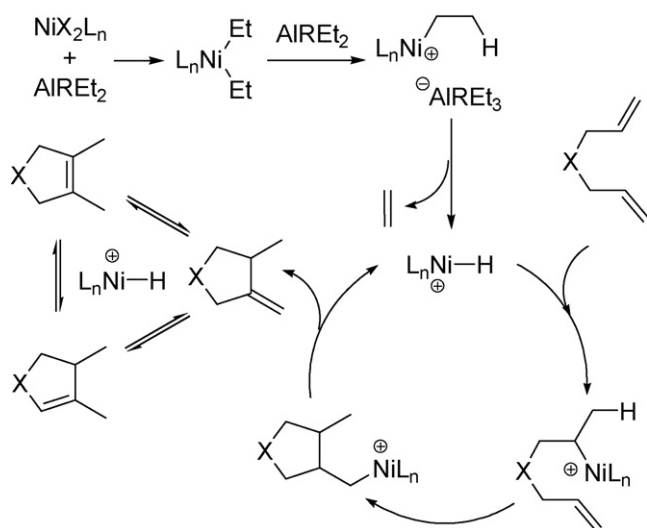
step is regenerated the nickel-hydride, which can enter the catalytic cycle again. In this way a methyl(methylene)cycloalkane derivative is the primary product. The formation of the double bond positional isomers can be easily explained by hydronickelation of the product followed by β -hydrogen elimination. Although speculative, the involvement of the nickel-hydride as the catalytically active species explains the formation of the observed products during cycloisomerization [13–15] and has been proposed in other related processes as well [23].

One of the possibilities to examine ligand effect in catalytic cycloisomerization is to prepare the series of the corresponding Ni(II) catalysts individually. However, we became intrigued whether it is possible to design a simpler catalytic system using organic solvent soluble Ni(II) salts that upon addition of ligands would give rise to the corresponding complexes “in situ”. Under such conditions screening of various ligands and the comparison of the catalytic activity and product selectivity of both catalytic systems could provide desired information.

2. Experimental

2.1. General

Solvents were dried by standard methods (THF, toluene: Na-benzophenone; dichloromethane: CaH₂) and distilled under argon before use. All other reagents were obtained from com-



Scheme 2. The proposed mechanism of Ni(II)/Et₂AlCl catalyzed cycloisomerization of 1,6-heptadienes.

mercial sources and used without further purification. GC analyses were obtained on a Shimadzu GC-17A chromatograph equipped with a Zebtron ZB-5 column (5% phenyl–95% dimethyl polysiloxane). ¹H and ¹³C NMR spectra were recorded as CDCl₃ solutions on a Varian UNITY 400 INOVA instrument (¹H at 400 MHz, ¹³C at 100 MHz) with Me₄Si as an internal standard. Mass spectra were obtained on a FINNIGAN MAT INCOS 50 instrument. Ni-catalyzed reactions were carried out under argon atmosphere in oven-dried Schlenk tubes. Yields were determined by the means of ¹H NMR with mesitylene as an internal standard. Starting compounds **1a–1c**, **6** [21,22], and **10** [24], NiBr₂(PPh₃)₂ and NiBr₂(PPh₃)₂ [25], and NiBr₂(BINAP) [26] complexes were prepared according to previously published procedures.

2.2. General procedure for Ni(OEtHex)₂/phosphine catalyzed cyclization

To a solution of a diene **1** (0.5 mmol) was added the Ni(OEtHex)₂ (8.0 mg; 0.025 mmol) and a phosphine (0.05 mmol for monodentate and 0.025 for bidentate phosphine) in dry toluene (3 mL), and 1.8 M solution of Et₂AlCl in toluene (55 μ L, 0.1 mmol) under argon in an oven-dry Schlenk tube. The reaction mixture was stirred at room temperature (within 20–25 °C) for appropriate amount of time. Then it was quenched with a portion of water (1 mL) followed addition of 3 M solution of HCl (3 mL) and extracted with hexane (3 \times 3 mL). Organic phase was separated and dried (MgSO₄). The product was filtered on a short silica gel column and evaporated.

Spectral characteristics of the formed products such as diethyl 3-methyl-4-methylenecyclopentane-1,1-dicarboxylate **2a** [12b], diethyl 3,4-dimethylcyclopent-2-ene-1,1-dicarboxylate **3a** [18c], diethyl 3,4-dimethylcyclopent-3-ene-1,1-dicarboxylate **4a** [18a], diethyl (prop-2-en-1-yl)(prop-1-en-1-yl)propandioate **5a** [28], 3-methylene-4-methylspiro[cyclopentane-1,3'-coumaran-2-one] **2b** [22], 3-methylene-4-methylspiro(cyclopentane-1,9'-fluorene) **2c** [5d,22], 3,4-dimethylspiro[cyclopent-3-ene-1,9'-fluorene] **3c** and 3,4-dimethylspiro[cyclopent-2-ene-1,9'-fluorene] **4c** [22], diethyl (*E*)-3-ethenyl-4-methylcyclopentane-1,1-dicarboxylate **7** [27] were in agreement with the previously reported data.

2.3. Diethyl

(*E*)-(but-2-en-1-yl)-(*E*)-(prop-1-en-1-yl)propandioate (**8**)

Characteristic signals are 5.60 (dq, *J* = 16, 6.4 Hz, 1H) for CH₃–CH = CH–C(COOEt)₂R and 5.91 (dq, *J* = 16, 1.7 Hz, 1H) for CH₃–CH = CH–C(COOEt)₂R.

3. Results and discussion

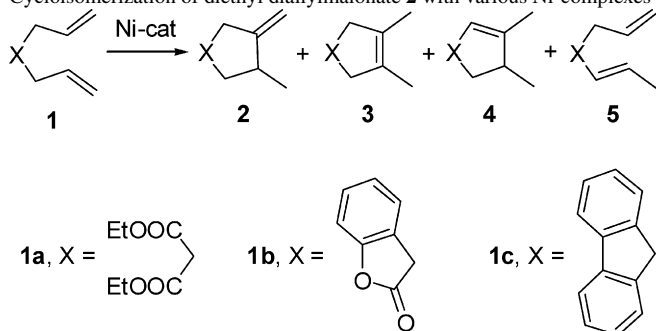
At the outset, the problem of finding organic solvent soluble Ni-salt had to be solved. Within this context, we found that the commercially available Ni(2-ethylhexanoate)₂ (abbreviated to Ni(OEtHex)₂), which is soluble in common organic solvents including toluene, suited our purpose well. Thus simple stirring of a toluene solution of Ni(OEtHex)₂ with the appropriate lig-

and at room temperature resulted in the clean formation of the corresponding Ni(II)/ligand complexes.

Next, we decided to screen the catalytic activity of the Ni(OEtHex)₂/phosphine/Et₂AlCl system in toluene at room temperature on the course of cycloisomerization of 1,6-heptadienes **1a–1c** (Table 1). Et₂AlCl was chosen as the reductant because it showed better properties in comparison with Et₃Al for cycloisomerization of 1,6-heptadienes [22]. Generally, the formation of four products was observed during the course of reaction: three cyclopentane regioisomers **2–4** and a product of the double bond migration **5**. The cycloisomerization carried out in the presence of triphenylphosphine (Entry 1) gave rise selectively to **2a** in high 96% yield within 1.5 h. For comparison was also done the reaction in the presence of NiBr₂(PPh₃)₂, which also afforded selectively **2a** in 99% yield in 1 h (Entry 2). Obviously, both catalytic systems have the same efficiency. The use of the catalytic system based on the use of triphenylphosphine derivatives bearing electron-donating (MeO) and electron-withdrawing groups (CF₃) gave quite different results. In the former case (Entry 3), the reaction was finished within 1 h giving **2a** in high yield (87%) and selectivity. In the latter case (Entry 4), the reaction almost did not proceed

(**2a**, <2%) even after a prolonged reaction time (24 h). The use of tributylphosphine led selectively to **2a** as well, but only in 75% yield after prolonged reaction time of 24 h (Entry 5). This observation was rather surprising, because we previously reported that the reaction catalyzed by NiBr₂(PBU₃)₂ gave **2a** in 92% yield in just 1 h [22]. Application of ferrocenyl(diphenyl)phosphine provided **2a** selectively in high 90% yield (Entry 6). The use of trisfurylphosphine (Entry 7) gave a mixture of **2a** (20%) and **5a** (15%). A sterically hindered ligand, tris(*o*-tolyl)phosphine (Entry 8), provided a mixture of **2a** and **3a** (7% and 5%) only after considerably prolonged reaction time of 24 h. The use of triphenylphosphite and triphenylphosphine oxide did not yield any detectable amounts of cyclized products even after 3 days reaction time (Entries 9 and 10). Low yield of **2a** (20%) was also observed in the presence of triphenylarsine (Entry 11). As for the bidentate phosphines the combination with DPEPhos gave rise to a mixture of **2a**, **3a**, and **4a** in 15, 5, and 5% yields, respectively in 1h reaction time (Entry 12). Interestingly, further stirring of the reaction mixture for additional 24 h did not lead to any improvement of the reaction yields. Surprisingly, the use of other bidentate ligands such as FcPPh₂(NMe₂) and BINAP did not yield any products after 24 h reaction time

Table 1
Cycloisomerization of diethyl diallylmalonate **2** with various Ni-complexes and Et₂AlCl



Entry	1	Catalytic system	R.t (h)	Product (%) ^a			
				2	3	4	5
1	1a	Ni(OEtHex) ₂ /2PPh ₃	1.5	96			
2	1a	NiBr ₂ (PPh ₃) ₂	1	99			
3	1a	Ni(OEtHex) ₂ /2(4-MeOPh) ₃ P	1	87			
4	1a	Ni(OEtHex) ₂ /2(4-CF ₃ Ph) ₃ P	24	<2			
5	1a	Ni(OEtHex) ₂ /2PBu ₃	24	75			
6	1a	Ni(OEtHex) ₂ /2FcPPh ₂	15	90			
7	1a	Ni(OEtHex) ₂ /2P(2-furyl) ₃	2.5	20			15
8	1a	Ni(OEtHex) ₂ /2P(<i>o</i> -tolyl) ₃	24	7	5		
9	1a	Ni(OEtHex) ₂ /2P(OPh) ₃	72	n.r.			
10	1a	Ni(OEtHex) ₂ /2P(O)Ph ₃	20	n.r.			
11	1a	Ni(OEtHex) ₂ /2AsPh ₃	100	20			
12	1a	Ni(OEtHex) ₂ /DPEPhos	24	15	5	5	
13	1a	Ni(OEtHex) ₂ /FcPPh ₂ (NMe ₂)	24	n.r.			
14	1a	Ni(OEtHex) ₂ /BINAP	120	10 ^b			
15	1b	Ni(OEtHex) ₂ /2PPh ₃	1.5	99			
16	1b	NiBr ₂ (PPh ₃) ₂	1.5	99			
17	1c	Ni(OEtHex) ₂ /2PPh ₃	1.5	40	20	20	10
18	1c	NiBr ₂ (PPh ₃) ₂	1.5	70	18	11	

Reaction conditions Ni(OEtHex)₂ (0.05 equiv.), ligand (2 equiv., monodentate; 1 equiv., bidentate), Et₂AlCl (0.2 equiv.), toluene.

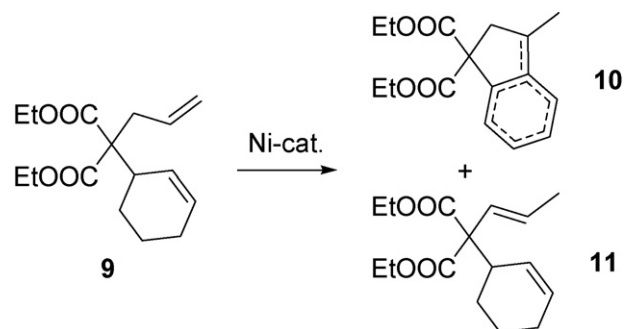
^a ¹H NMR or GC yields.

^b After 24 h the formation of cyclized products was not observed.

(Entries 13 and 14). In the latter case, **2a** was formed in low yield of 10% after 5 days. The situation did not improve even when preformed NiBr₂(BINAP) was used. The cycloisomerization of diallylcoumaranone **1b** proceeded uneventfully in the presence of triphenylphosphine giving product **2b** selectively in 99% yield in 1.5 h (Entry 15). The same result was obtained when NiBr₂(PPh₃)₂ was used as the catalyst (Entry 16). The reaction of diallylfluorene **1c** resulted in the formation of a mixture of **2c**, **3c**, **4c**, and **5c** in 40, 20, 20, and 10% yields, respectively (Entry 17). Substitution of Ni(OEtHex)₂/2PPh₃ for NiBr₂(PPh₃)₂ gave rise also a mixture of the same products **2c–4c**, but in 70%, 18%, and 11% yields, respectively (Entry 18).

The cycloisomerization of diethyl [(*E*)-buten-1-yl]allylmalonate **6** (Table 2) gave in most cases a mixture of cyclized product **7** and a product of the double bond migration **8**. The formation of the indicated regioisomeric product **7** can be rationalized by initial hydronicellation by the presumed nickel-hydride intermediate of the less substituted double bond, followed by intramolecular carbometallation and β-hydrogen elimination. The reaction carried out with triphenylphosphine proceeded slowly but almost quantitatively within 24 h affording a mixture of **7** (33%) and **8** (66%) (Entry 1). When PBu₃ was used, traces of the products were not detected even after 2 days (Entry 2). In the presence of P(*c*-Hex)₃ only the double bond migration was observed yielding **8** (20%) after 3 days (Entry 3). On the other hand, the cycloisomerization was also tested with NiBr₂(PPh₃)₂ and NiBr₂(PBu₃)₂. By using the first complex a mixture of **7** (45%) and **8** (30%) was obtained also after 3 days (Entry 4). The second complex afforded the same products in 50% yield each in just 18 h (Entry 5). In this regard, it should be noted that Ni-catalyzed cycloisomerization had reasonably high selectivity for the formation of **7**, whereas Pd-catalyzed [17] or Ru-catalyzed [6,7] reactions afford cyclized products with the different position of the double bond.

In an analogical manner proceeded the cyclization of diethyl cyclohex-2-en-1-yl)allylmalonate **9** (Scheme 3). According to ¹H NMR and GC analysis of the reaction mixture the starting compound was fully converted into an inseparable mixture of cyclized products. The direct assignment of signals to individ-

Scheme 3. Cycloisomerization of **9**.

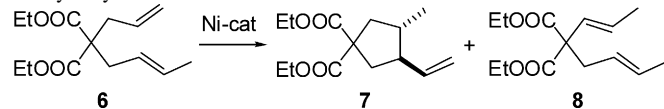
ual compounds was not possible, because the obtained spectra were superposition of signals belonging to the structurally similar compounds. According to ¹H NMR spectra typical signals of the terminal double bond disappeared (4.9–5.1 ppm) and new signals characteristic for the internal double bonds appeared (5.5–5.9 ppm). The formation bicyclic products, probably a mixture of the double bond positional isomers **10**, were identified by characteristic signals of methyl groups attached to a carbocycle, which had doublets in a region of 0.95–1.05 ppm. GC analysis indicated disappearance of the starting material and formation of at least four major products in a ratio of about 13:50:21:12 ratio. Unfortunately, attempts to control the product selectivity by changing of reaction temperature or time were not met with success. (Formation of one of the possible products was reported by Heumann et al. [17b], but spectral characteristics were not given.) As for the other products, compound **11** was identified by characteristic signals of vinylic C–H bond (5.84, dq, *J* = 16, 1.2 Hz) and of methyl group attached to the double bond (1.75, dd, *J* = 6.4, 1.6 Hz). The same result of cycloisomerization was obtained also in NiBr₂(PPh₃)₂ catalyzed reaction.

Last but not least, we observed that the course of the cycloisomerization, i.e. reaction times, product yields, and isomeric purity of the products, may depend on the actual Ni/Al ratio and a supplier of diethylaluminum chloride. Since the quality of diethylaluminum chloride depends on the amount of impurities, the reaction conditions, especially the reaction times, should be optimized for individual batch of it.

4. Conclusion

In summary, we have demonstrated that the catalytic systems comprising of Ni(OEtHex)₂ (5 mol%)/ligand (10 mol%)/Et₂AlCl (20 mol%) were able to affect the cycloisomerization of various 1,6-heptadienes into the corresponding cyclopentane derivatives. Out of various ligand systems the best results were obtained with the one using triphenylphosphine. It had a good catalytic activity for converting the starting diene into the cyclopentane derivatives and good to excellent selectivity for the formation of the corresponding methyl(methylene)cyclopentane derivatives **2** depending on the structural features of the 1,6-diene. In addition, a valuable information was also obtained in the cycloisomerization of the 1,6-octadiene, which proceeded with

Table 2

Catalytic cycloisomerization of **6**

Entry	Catalytic system ^a	R.t (h)	Product (%) ^b	
			7	8
1	Ni(OEtHex) ₂ /2PPh ₃	24	33	66
2	Ni(OEtHex) ₂ /2PBu ₃	48	–	–
3	Ni(OEtHex) ₂ /2P(<i>c</i> -Hex) ₃	60	–	20
4	NiBr ₂ (PPh ₃) ₂	60	45	30
5	NiBr ₂ (PBu ₃) ₂	18	50	50

^a Reaction conditions Ni(OEtHex)₂ (0.05 equiv.), ligand (2 equiv., monodentate; 1 equiv., bidentate), Et₂AlCl (0.2 equiv.), toluene.

^b ¹H NMR or GC yields.

high *trans*-stereoselectivity and reasonable selectivity for the formation of the methyl(vinyl)cyclopentane derivative **7**.

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