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Preliminary communication

[2 + 2] Dimerization of norbornadiene and its derivatives in the presence of nickel complexes and zinc metal

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Abstract

Norbornadiene undergoes [2 + 2] reaction in THF in the presence of NiX_2 and zinc metal powder to give an exo-*trans*-exo dimer and an exo-*trans*-exo-*trans*-exo trimer. In these products, the norbornadiene molecules are linked to each other by forming cyclobutane rings with all cyclobutane carbons occupying exo positions relative to the bridging carbons on the two norbornadiene fragments. Polymerization of norbornadiene occurs if the catalyst NiX_2 is replaced by $Ni(PPh_3)_2Cl_2$. 1,4-Dihydro-1,4-epoxynaphthalene, 5,8-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene, 5-methoxy-1,4-dihydro-1,4-epoxynaphthalene and methyl 1,4-dihydro-1,4-iminonaphthalene-9-carboxylate also dimerize to give exo-*trans*-exo products in excellent yields in toluene in the presence of $Ni(PPh_3)_2Cl_2$ and Zn powder. For the dimerization products of 5-methoxy-1,4-dihydro-1,4-epoxynaphthalene, *cis* and *trans* isomers with respect to the orientation of methoxy groups in about 1 : 1 ratio were observed. Under similar reaction conditions for the dimerization of norbornadiene, norbornene undergoes reductive dimerization to afford a product which consists of two norbornyl groups. The structure of this product is also exo-*trans*-exo.

Keywords: Nickel; Dimerization; Zinc

1. Introduction

Norbornadiene and its analogs are known to undergo various types of metal-catalyzed dimerizations and oligomerizations [1–21] due to facile coordination to metal centers with various coordination modes of these organic compounds. The products that possess a high ratio of carbon to hydrogen atoms and multiple rings are potentially useful as energetic fuel [22–24]. One of these reactions is the [2 + 2] dimerization that is thermally impossible in the absence of a metal catalyst. Several metals including iron [8,25], cobalt [17], rhodium [3–7] and nickel [26] are reported to catalyze the [2 + 2] dimerization of norbornadiene. Nickel systems known to catalyze dimerization are $Ni(CO)_4$ [11], $NiCl_2(PBu^n_3)_2$-$NaBH_4$ [12], $Ni(CO)_2(PPh_3)_2$ [13] and Ni vapor [19]. There are six possible products, **1-I–1-VI**, for the [2 + 2] dimerization of norbornadiene. Both exo and endo products were observed for $Ni(CO)_4$, $NiCl_2(PBu^n_3)_2$-$NaBH_4$ and $Ni(CO)_2(PPh_3)_2$. Only nickel vapor selectively dimerizes norbornadiene to the exo-*trans*-exo product, **1-I**, but in low yield.

We are interested in use of MX_2–zinc (M = Co, Ni and Pd) in the presence of phosphine as catalyst systems for organic reactions [27]. These systems may conveniently generate low-valent and unsaturated metal species that are not readily available by conventional synthetic methods. In this paper, we describe the use of $NiX_2(PPh_3)_2$-zinc systems in catalysis of [2 + 2] reactions of norbornadiene and its derivatives. The nickel systems are not only highly effective, but also show great stereo selectivity for the dimerization of norbornadiene and 7-heteroatom norbornadienes.

2. Results and discussion

2.1. [2 + 2] Reaction of norbornadiene

In the presence of NiX_2 (X = Cl and Br) and zinc metal, norbornadiene undergoes [2 + 2] reaction in THF at ambient temperature. The initial product of the catalysis is the [2 + 2] dimer (**1-I**) of norbornadiene.

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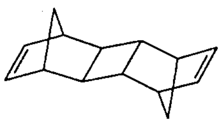
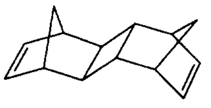
As the reaction proceeds, the dimer further reacts with norbornadiene to afford a trimerization product (**2**). The product mixture which contains both dimer and trimer at the end of the reaction may be separated by sublimation. Under similar reaction conditions, this norbornadiene dimer reacts further with norbornadiene to yield the trimer. However, attempts to synthesize a tetramer from the reaction of the trimer with norbornadiene in the presence of $NiBr_2$ and zinc metal in THF were unsuccessful.

The structure assignments of the dimer and trimer are based on mass and ^1H and ^{13}C NMR spectra of these compounds. For the dimer, there are five proton signals with one of them an olefin–proton resonance in the ^1H spectrum. In the ^{13}C NMR spectrum, only four signals, including an olefin carbon resonance, were observed. Four (**1-I**, **1-III–IV**) of the six possible [2 + 2] isomers would show the same number of signals in the NMR spectra as those of the dimer. Because the protons on the bridge head and on the four-membered ring of the dimer do not couple with each other, the endo-*trans*-endo (**1-IV**) and endo-*cis*-endo (**1-III**) isomers of these four structures are ruled out. For an endo-*trans*-endo or endo-*cis*-endo isomer, a coupling constant of ca. 5.0 Hz is expected between the proton on a bridgehead and the neighboring exo proton on the four-membered ring [28]. Either exo-*trans*-exo (**1-I**) or exo-*cis*-exo (**1-V**) isomers cannot be excluded as a possible structure based on the number of resonances, chemical shifts and coupling patterns. A dimerization product assigned as the exo-*trans*-exo isomer (**1-I**) according primarily to the observed ^1H NMR data [1] was prepared previously from norbornadiene catalyzed by $Co_2(CO)_6(PPh_3)_2$. Comparison of the present ^1H NMR data with those reported [1] lead us to assign an exo-*trans*-exo structure for the dimerization product of norbornadiene in the presence of NiX_2 and zinc metal. The results of X-ray structure determination of the dimer of 1,4-epoxy-1,4-dihydronaphthalene (vide infra) further support the exo-*trans*-exo structure.



1-I



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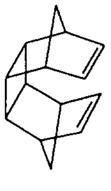

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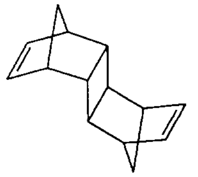

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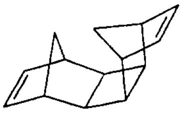
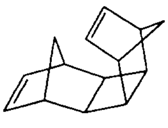
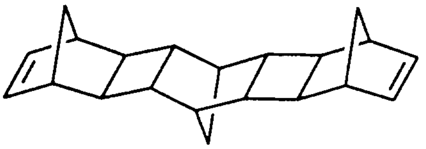


1-V



1-VI

The NMR spectra of the trimerization product show eight proton and seven carbon resonances indicating that the species is highly symmetric. Only one olefin proton and one olefin carbon signals are observed in these spectra. The number of NMR signals and their relative intensities are consistent with a structure of either exo-*trans*-exo-*trans*-exo or exo-*cis*-exo-*cis*-exo arrangements, but the lack of coupling between the two types of protons on the cyclobutane rings supports that the protons are in trans positions and that the trimer product is exo-*trans*-exo-*trans*-exo. Yields of both dimer and trimer depend greatly on the solvent and the ligand employed. Highest yields (dimer, 61%; trimer, 28%) were obtained from the reaction carried out in THF at room temperature using $NiBr_2$ and zinc metal powder as the catalyst system. The $NiCl_2$–Zn system was less reactive giving 44% of dimer and 5% trimer under similar conditions. We have noticed that nickel chloride is much less soluble than nickel bromide in THF. The solubility of catalyst likely accounts for the observations that $NiCl_2$–Zn is less reactive than $NiBr_2$–Zn. The catalytic activity of the $NiBr_2$–Zn system in a less polar solvent such as ether or toluene is much lower than in THF due to the low solubility of nickel bromide in these solvents. Although the solubility of nickel bromide is much higher in acetonitrile, DMF or DMSO than in THF, the catalytic activity of the $NiBr_2$–Zn system in these solvents is lower than in THF. The greater coordinating abilities of these solvents prevent norbornadiene from being associated to the nickel center and thus diminish the catalytic activity. The addition of triphenylphosphine to $NiBr_2$–Zn system inhibited the [2 + 2] reaction and led to polymerization of norbornadiene.



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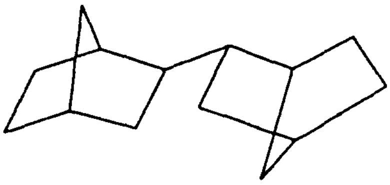
2.2. *Reductive dimerization of norbornene*

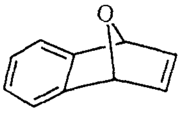
Under similar conditions to the catalytic [2 + 2] reaction of norbornadiene, norbornene was converted into a partial hydrogenation product **3** consisting of two norbornenes and a hydrogen molecule. Addition of a small amount of water increased the yield of **3**. The ^{13}C NMR spectrum of this product exhibits three tertiary carbon and four secondary carbon signals, while the ^1H NMR spectrum shows broad resonances in the region δ 0.9 ~ 2.2. There is no resonance corresponding to an olefin proton or carbon in the ^1H and ^{13}C NMR spectra. Similar to the [2 + 2] dimer of norbornadiene, the NMR spectra are in accord with either the exo-*trans*-exo or exo-*cis*-exo structure. In view of the similarity of norbornadiene and norbornene and the structure of the observed norbornadiene dimer, we assign the structure of product **3** to be exo-*trans*-exo.



3

2.3. Dimerization of 1,4-dihydro-1,4-epoxynaphthalene (4) and its derivative

Similar to norbornadiene, 1,4-dihydro-1,4-epoxynaphthalene undergoes [2 + 2] dimerization in the presence of nickel catalyst to give **5**. Owing to the nature of the reactant, there is no trimerization product observed at the end of the reaction. The $NiBr_2$–Zn in THF also catalyzed this [2 + 2] dimerization at ambient temperature, albeit in low yield. Raising the reaction temperature did not increase the yield, but led to decomposition of the nickel complex to nickel metal. If the reaction was carried out in the presence of $NiCl_2(PPh_3)_2$ and Zn in toluene at 60°C, the reaction time for the catalysis was greatly shortened and a higher yield (96%) of the dimer **5** was obtained. The presence of PPh_3 ligand appears to prevent the nickel catalyst from being decomposed to the inactive nickel metal. It should be noted that norbornadiene does not dimerize but undergoes polymerization in the presence of $NiCl_2(PPh_3)_2$ in toluene and in THF.



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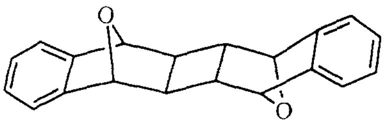
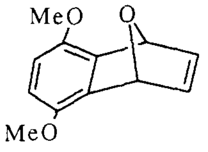


5

The ^1H and ^{13}C NMR spectra of this dimer consisting of four and five resonances, respectively, are in agreement with an exo-*trans*-exo or an exo-*cis*-exo structure. The crystal structure of this product was determined by X-ray diffraction and the results confirm that this compound contains two molecules of 1,4-dihydro-1,4-epoxynaphthalene which are linked to each other by forming a cyclobutane ring between the carbon–carbon double bonds in each molecule and the two 1,4-dihydro-1,4-epoxynaphthalene molecules are *trans* to each other with an exo-*trans*-exo configuration.

Similar to 1,4-dihydro-1,4-epoxynaphthalene, 5,8-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene (**6**) dimerizes readily in the presence of $NiCl_2(PPh_3)_2$–Zn in toluene to give **7** in excellent yield. The ^1H and ^{13}C NMR spectra of the product which consist of four and six signals, respectively, and the absence of coupling between the protons on the bridgehead and on the 4-member ring support that the structure is exo-*trans*-exo.



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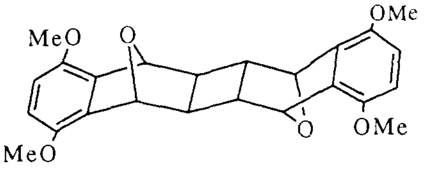
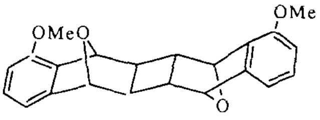
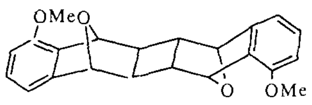


7

The $NiCl_2(PPh_3)_2$–Zn system also catalyzes the [2 + 2] dimerization of 5-methoxy-1,4-dihydro-1,4-epoxynaphthalene in toluene. As expected, the product of this reaction contains *cis* (**8a**) and *trans* (**8b**) isomers in about 1 : 1 ratio. Addition of hexanes to the product mixture in dichloromethane led to precipitation of one of the isomers. The remaining solution was evaporated and the residue was separated on a silica-gel column to give a mixture that contained mainly the other isomer (isomer ratio ≅ 10 : 1). Owing to similarity in properties, the structures of these isomers are difficult to assign. Both products have the same number of ^1H and ^{13}C NMR signals and almost identical chemical shifts. Fortunately, the splitting patterns of the protons on the cyclobutane ring are quite different. A pair of doublet of doublets was observed for the cyclobutane protons of the isomer precipitated from hexanes, while a pair of doublets was recorded in the NMR spectrum of the other isomer. Based on the structures of these isomers, we expect the trans isomer to exhibit a pair of doublet of doublets for the protons on the cyclobutane due to coupling with a *cis* proton and a *trans* proton. For the *cis* isomer, each proton on the cyclobutane is expected to be coupled by only a *cis* neighboring proton and a pair of doublets should be observed for the protons on cyclobutane ring. The two *trans* protons on the same side of the methoxy groups on the cyclobutane of a *cis* isomer are identical in magnetic environment and do not couple to each other. Analogously, no coupling for the other pair of *trans* protons opposite to the methoxy groups is expected to be observed. As a result, the isomer precipitated from dichloromethane and hexanes is *trans*, while the other isomer is *cis*.



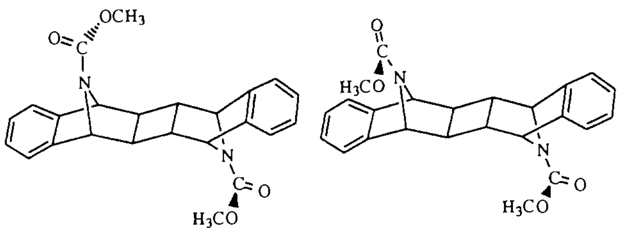
8a



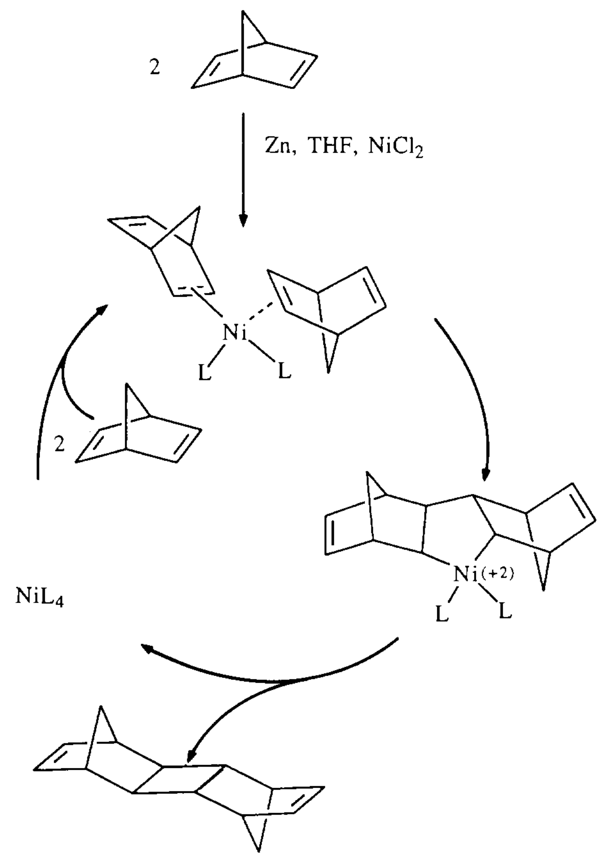
8b

2.4. Dimerization of methyl 1,4-dihydro-1,4-iminonaphthalene-9-carboxylate

In the presence of $NiCl_2(PPh_3)_2$ and zinc metal, methyl 1,4-dihydro-1,4-iminonaphthalene-9-carboxylate undergoes homo [2 + 2] reaction in toluene solution to give the exo-*trans*-exo dimer **9** in 77% isolated yield. This homo coupling was carried out at 90°C, higher than the temperature for norbornadiene and 1,4-dihydro-1,4-epoxynaphthalene and its derivatives. In the ^1H NMR spectrum, the proton resonances for the cyclobutane ring, methyl group, bridgehead, and phenylene groups appear at δ 2.08, 3.59, 5.12, and 7.14 and 7.25, respectively. A slight broadening of the bridgehead signal at δ 5.12 was observed. The absence of coupling between protons on the bridgehead and on the cyclobutane ring supports that the structure of this dimer is exo-*trans*-exo. The ^{13}C NMR spectrum of this product at ambient temperature is surprisingly complicated. The resonances of the carbons of the bridgehead, cyclobutane ring and phenylene all appear as broad multiplets. These NMR results may be rationalized on the basis of the presence of two isomers arising from the partial double bond character of C–N bond in the carbamate groups and the planarity of the carbamate groups. The observed broad ^{13}C signals indicates that the C–N bond in the carbamate group rotates at ambient temperature at a rate significant on the NMR time scale.



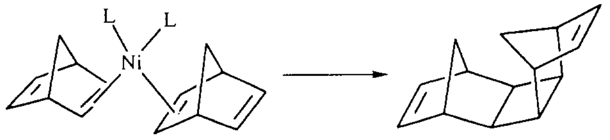
9



Scheme 1.

2.5. Mechanism of [2 + 2] reaction

In spite of the lack of information on the catalytic intermediates of the present [2 + 2] coupling reactions, the mechanism for the catalysis is proposed based on known nickel chemistry and established principles of organometallic chemistry. As shown in Scheme 1, the observed catalysis is initiated by the reduction of nickel halide to a Ni(O) species. Coordination of two norbornadiene molecules, followed by coupling of these two coordinated ligands affords a metallacyclopentane intermediate. Reductive elimination of this species leads to the dimerization product and a Ni(O) intermediate. The stereochemistry of the product depends on how the norbornadiene ligands are coordinated to the nickel center. It is clear that exo coordination is necessary in order to obtain the exo products. There are two conformations for exo coordination of two norbornadiene molecules to the nickel center as shown in Scheme 1 and Eq. (1). The exo-*trans* conformation (Scheme 1) is expected to give an exo-*trans* product, while the exo-*cis* intermediate in Eq. (1) should afford an exo-*cis* product after reductive elimination of the metallacyclopentane intermediate. A metallacyclopentane complex of nickel $Ni(bpy)(NBD)_2$ (NBD = norbornadiene) was successfully synthesized and its structure was determined by X-ray diffraction to be an exo-*trans*-endo metallacyclopentane [19]. Heating this complex led to formation of a [2 + 2] dimer with the expected exo-*trans* endo structure. Related work on the synthesis of nickelacyclopentane from nickel complexes and two olefin molecules is also known [19,29–50]. Catalytic formation of the exo-*trans*-exo-*trans*-exo trimer of norbornadiene is expected to follow similar pathways to those shown in Scheme 1. Apparently, this



(1)

trimer arises from further reaction of norbornadiene with the exo-*trans*-exo dimer. While the mechanisms for [2 + 2] dimerization of 1,4-dihydro-1,4-epoxynaphthalene, 5,8-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene, 5-methoxy-1,4-dihydro-1,4-epoxynaphthalene and methyl 1,4-dihydro-1,4-iminonaphthalene-9-carboxylate are also expected to be similar to that shown in Scheme 1, the presence of heteroatoms at bridging positions of these substrates appears to enhance the yields of the reactions. Coordination of the electron lone pairs on the heteroatoms likely occurs during the course of catalysis and accounts for the enhanced yields.

3. Experimental section

All reactions were performed under dry nitrogen and all solvents were dried by standard methods. ^{1}H and ^{13}C NMR experiments were performed on a Varian Gemini 300 instrument at 300 MHz. IR spectra were obtained on a Bomem MB-100 spectrometer. Mass spectra at low and high resolutions were recorded on JEOL JMS-D100 and JMS-HX110 instruments, respectively.

The following chemicals were obtained from the indicated commercial suppliers and were used without further purification unless otherwise noticed: $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot nH_2O$ (Merck), $NiBr_2$(Merck), Ni(acac)$_2$ (Merck), norbornadiene (Merck), norbornene (Aldrich), 1,4-dihydro-1,4-epoxynaphthalene (Aldrich), triphenylphosphine (Janssen) and zinc metal powder (Merck). Anhydrous $NiCl_2$ and $CoCl_2$ were obtained by heating $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot nH_2O$ at 150°C for 24 h. 5,8-Dimethoxy-1,4-dihydro-1,4-epoxynaphthalene, 5-methoxy-1,4-dihydro-1,4-epoxynaphthalene, methyl-1,4-dihydro-1,4-iminonaphthalene-9-carboxylate [51] and $NiCl_2(PPh_3)_2$ [52] were prepared according to published procedures.

3.1. *Dimerization and trimerization of norbornadiene catalyzed by nickel halide and zinc metal*

A round-bottom flask containing $NiBr_2$ (0.437 g, 2.00 mmol) and zinc powder (1.00 g, 15.3 mmol) was purged with nitrogen three times. To the flask were added sequentially norbornadiene (3.68 g, 40.0 mmol), and THF (10.0 ml). The mixture was then stirred at 50°C for 72 h. On cooling to room temperature, methylene chloride (20–30 mL) was added to the reaction solution, and the mixture was stirred in the air for 1 h. After filtration through Celite, the filtrate was concentrated on a rotary evaporator to afford a white solid. The solid was redissolved in THF and to the solution was added ethanol to precipitate selectively the polymer in the THF solution. The filtrate was evaporated and the residue was sublimed at 48°C and at 0.2 mm Hg to afford the dimer as pale yellow crystals (2.24 g, 61%). Important spectral data for the dimer: ^{1}H NMR (300 MHz, $CDCl_3$)δ 6.02 (s, 4 H, = –H), 2.63 (s, 4 H, bridgehead), 1.70 (d, $J = 9.0$ Hz, 2 H, bridge), 1.35 (s, 4 H, cyclobutane), 1.23 (d, $J = 9.0$ Hz, 2 H, bridge); ^{13}C {^{1}H} (300 MHz, $CDCl_3$)δ 136.21 (d), 44.05 (d), 42.22 (t), 39.56 (d); MS (*m/z*, (%)) 184 (M^+, 24.0), 118 ($[M-C_5H_6]^+$, 84.0), 92 ($[M-C_7H_8]^+$, 100); M^+ calcd for $C_{14}H_{16}$ 184.1253, found 184.1246.

Recrystallization of the residue from sublimation from hexane gave the trimer as white powder (1.00 g, 27%). ^{1}H NMR (300 MHz, $CDCl_3$)δ 5.94 (s, 4 H, = –H), 2.60 (s, 4 H, bridge), 1.90 (s, 2 H, bridgehead), 1.73 (d, $J = 9.0$ Hz, 2 H, bridge), 1.72 (s, 2 H, bridge), 1.39 (s, 4 H, cyclobutane), 1.31 (s, 4 H, cyclobutane), 1.15 (d, 2 H, bridge); ^{13}C{^{1}H} (300 MHz, $CDCl_3$)δ 135.51 (d), 44.22 (d), 41.86 (d), 41.61 (d), 41.58 (t), 40.64 (d), 28.94 (t); MS (*m/z*, (%)) 276 (M^+, 28.0), 184 ($[M-C_7H_8]^+$, 25.1), 118 (80.0), 92 ($[C_7H_8]^+$, 100); M^+ (*m/z*) calcd for $C_{21}H_{24}$ 276.1879, found 276.1869.

3.2. *Reductive coupling of norbornene catalyzed by nickel halide*

A round-bottom flask containing norbornene (3.76 g, 40.00 mmol), $NiCl_2(PPh_3)_2$ (0.900 g, 1.38 mmol) and zinc powder (1.00 g, 15.3 mmol) was purged with nitrogen four times. To the flask was added water (0.72 g, 40 mmol) and the mixture was then stirred at 45°C for 24 h. Methylene chloride (20 ml) was added to the reaction solution, and the mixture was stirred in the air for 1 h. The mixture was filtered through Celite and the filtrate was concentrated on a rotary evaporator to afford the crude product as a colorless liquid in 19% (0.707 g). ^{1}H NMR (300 MHz, $CDCl_3$)δ 2.12 (br s, 2 H), 2.03 (br s, 2 H bridgehead), 1.53 (br s, 2 H), 1.44 (br m, 4 H), 1.26 (br m, 6 H), 1.01 (br m, 6 H); ^{13}C{^{1}H} NMR (300 MHz, $CDCl_3$)δ 48.36 (d), 40.92 (d), 36.86 (d), 36.25 (t), 35.75 (t), 30.50 (t), 29.22 (t); MS (*m/z*, (%)), 190 (M^+, 100), 95 ($[M-C_7H_{11}]^+$, 24.0); M^+ calcd for $C_{14}H_{22}$ 190.1722, found 190.1718.

3.3. *Dimerization of 1,4-dihydro-1,4-epoxynaphthalene catalyzed by $Ni(Cl)_2(PPh_3)_2$ and zinc metal*

A round-bottom flask containing 1,4-dihydro-1,4-epoxynaphthalene (0.144 g, 1.00 mmol), $Ni(Cl)_2(PPh)_2$ (0.0350 g, 0.0500 mmol), and zinc powder (0.180 g, 2.75 mmol) was purged with nitrogen three times. Into the flask was syringed toluene (1.0 ml) and the mixture was then stirred at 60°C for 10 h. The solution was evaporated and the residue was recrystallized from hexane to give the desired dimerization product in 96% yield (0.138 g). ^{1}H NMR (300 MHz, $CDCl_3$)δ 7.25 (dd, $J = 5.3$ Hz, $J = 3.3$ Hz, 2 H, benzo), 7.19 (dd, $J = 5.3$ Hz, $J = 3.3$ Hz, 2 H, benzo), 5.24 (s, 4 H, bridgehead), 2.14 (s, 4 H, endo-cyclobutane); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 MHz)δ 144.32 (s), 126.86 (d), 119.46 (d), 81.30 (d, O–C, bridgehead), 41.64 (d, cyclobutane); MS (*m/z* (%)) 288 (M^+, 33.0), 269 (24.0), 241 (20.4), 157 (23.6), 118 ($C_8H_6O^+$, 100); M^+ calcd for $C_{20}H_{16}O_2$ 288.1152, found 288.1133.

3.4. Dimerization of 5,8-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene catalyzed by $Ni(Cl)_2(PPh)_2$ and zinc metal

To a round-bottom flask containing 5,8-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene (0.204 g, 1.00 mmol), $Ni(Cl)_2(PPh)_2$ (0.0350 g, 0.0500 mmol) and zinc powder (0.180 g, 2.75 mmol) which was purged with nitrogen three times was added toluene (1.0 ml). The mixture was then stirred at 60°C for 10 h. On cooling to room temperature, dichloromethane (25 ml) was added to the system. The solution was filtered and the solvent was removed on a rotary evaporator. Recrystallization from hexane gave the desired dimerization product in 97% yield (0.196 g). ^1H NMR (300 MHz, $CDCl_3$)δ 6.63 (s, 4 H, benzo), 5.43 (s, 4 H, O–CH, bridgehead), 3.79 (s, 12 H, O–CH_3), 2.14 (s, 4 H, endo cyclobutane); $^{13}C\{^1H\}$ NMR (300 MHz, $CDCl_3$), 146.95 (s, benzo), 133.37 (s, benzo), 111.16 (d, benzo), 79.29 (d, O–C, bridgehead), 56.16 (q), 41.23 (d); MS (*m/z* (%)) 408 (M^+, 2.1), 382 ($[M-C_2H_2]^{+\cdot}$ 60.0), 353 (9.7), 305 (9.3), 291 (26.1), 204 (26.6), 178 ($C_{10}H_{10}O_3$, 39.5), 163 ($[C_{10}H_{10}O_3-CH_3]^{+\cdot}$ 57.3), 102 (100); M^+(*m/z*) calcd for $C_{24}H_{24}O_6$ 408.1575, found 408.1580.

3.5. Dimerization of 5-methoxy-1,4-dihydro-1,4-epoxynaphthalene catalyzed by $Ni(Cl)_2(PPh)_2$ and zinc metal

To a round-bottom flask containing 5-methoxy-1,4-dihydro-1,4-epoxynaphthalene (0.174 g, 1.00 mmol), $Ni(Cl)_2(PPh)_2$ (0.0350 g, 0.0500 mmol), and zinc powder (0.180 g, 2.75 mmol) which was purged with nitrogen three times, was added toluene (0.8 ml). The mixture was then stirred at 65°C for 16 h. Dichloromethane (25 ml) was then added to the system and the system was stirred under air for 1 h to decompose the nickel complex. The solution was filtered and the solvent was concentrated on a rotary evaporator. Addition of hexane to the solution gave a white precipitate which was collected affording the trans-form dimerization product in 48% yield (0.0850 g). The remaining solution was concentrated on a rotary evaporator, the residue was washed by hexane to remove triphenylphosphine and was then separated on a silica-gel column using dichloromethane and hexane (*v/v*, 5:3) as the eluent to afford the *cis*-form product in 50% yield (0.0865 g). Spectral data for the *trans* isomer: ^1H NMR (300 MHz, $CDCl_3$)δ 7.12 (t, $J = 7.3$ Hz, 2 H, benzo), 6.86 (d, $J = 7.3$ Hz, 2 H, methoxylbenzo), 6.70 (d, $J = 8.2$ Hz, 2 H, benzo), 5.43 (s, 2 H, bridgehead), 5.22 (s, 2 H, bridgehead), 3.84 (s, 6 H, OCH_3), 2.14 (dd, $J = 5.3$ Hz, $J = 2.4$ Hz, 2 H, cyclobutane), 2.10 (dd, $J = 5.3$ Hz, $J = 2.4$ Hz, cyclobutane); ^{13}C $\{^1H\}$ NMR (300 MHz, $CDCl_3$)δ 152.46 (s), 146.37 (s), 131.25 (s), 128.40 (d), 112.12 (d), 109.96 (d), 81.49 (d, O–C, bridgehead), 78.94 (d, O–C, bridgehead), 55.51 (q), 41.76 (d), 41.29 (d); MS (*m/z* (%)) 348 (M^+, 31.7), 315 (4.6), 301 (10.8), 271 (6.9), 148 (100), 115 (34.7); M^+ (*m/z*) calcd for $C_{22}H_{20}O_4$ 348.1363, found 348.1367.

Spectral data for the *cis* isomer: ^1H NMR (300 MHz, $CDCl_3$) δ 7.08 (t, $J = 7.4$ Hz, 2 H, benzo), 6.83 (d, $J = 7.4$ Hz, 2 H, benzo), 6.66 (d, $J = 8.3$ Hz, 2 H, benzo), 5.42 (s, 2 H, bridgehead), 5.18 (s, 2 H, bridgehead), 3.80 (s, 6 H, O–CH_3), 2.14 (d, $J = 5.8$ Hz, 2 H, cyclobutane), 2.07 (d, $J = 5.8$ Hz, cyclobutane); ^{13}C $\{^1H\}$ NMR (300 MHz, $CDCl_3$) δ 152.47 (s), 146.31 (s), 131.28 (s), 128.36 (d), 112.07 (d), 110.04 (d), 81.48 (d, O–C, bridgehead), 78.96 (d, O–C, bridgehead), 55.50 (q), 41.75 (d), 41.29 (d); MS (*m/z* (%)) 348 (M^+, 31.7), 315 (4.60), 301 (10.8), 271 (6.90), 148 (100), 115 (34.7); M^+ (*m/z*) calcd for $C_{22}H_{20}O_4$ 348.1363, found 348.1365.

3.6. Dimerization of Methyl 1,4-Dihydro-1,4-iminonaphthalene-9-carboxylate Catalyzed by $Ni(Cl)_2(PPh)_2$ and Zinc Metal

To a round-bottom flask containing methyl-1,4-dihydro-1,4-iminonaphthalene-9-carboxylate (0.201 g, 1.00 mmol), $Ni(Cl)_2(PPh)_2$ (0.035 g, 0.050 mmol), PPh_3 (0.0524 g, 0.20 mmol) and zinc powder (0.180 g, 2.75 mmol) which was purged with nitrogen three times was added toluene (1.0 ml). The system was then stirred at 90°C for 21 h. On cooling to room temperature, dichloromethane (25 ml) was added to dilute the solution. The solution was stirred under air for 1 h to quench the reaction. The solid in the system was filtered and the filtrate was evaporated to dryness. The residue was recrystallized from dichloromethane and hexane to afford the desired product in 77% yield (0.1542 g). ^1H NMR (300 MHz, $CDCl_3$) δ 7.14 (m, 4 H, benzo), 7.25 (m, 4 H, benzo), 5.12 (br s, 4 H, bridgehead), 3.59 (s, 6 H, O–CH_3), 2.08 (br s, 4 H, cyclobutane) ^{13}C $\{^1H\}$ NMR (300 MHz, $CDCl_3$) δ 156.16 (s, C=O), 144.10 (br s), 126.31 (d), 120.22 (br d), 62.90 (d, N–C, bridgehead), 52.12 (q), 42.35 (d); MS (*m/z*, (%)) 402 (M^+, 100), 328 ($[M-NCOOCH_3]^+$, 10.0); M^+ calcd for $C_{24}H_{22}O_4N_2$ 402.1581, found 402.1584. Anal. calcd for $C_{24}H_{22}O_4N_2$: C, 71.64; H, 5.47; N, 6.97. Found: C,71.15; H, 5.55; N, 6.70.

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