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# Nickel-Catalyzed Regio- and Stereoselective Homo 1,4-Dialkenylation of Conjugated Dienes.

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Abstract: 2,3-Dimethyl-1,3-butadiene and cyclic dienes react with  $\beta$ -iodoenones (RI: 3-Iodo-2-cyclohexen-1one, 5,5-dimethyl-3-iodo-2-cyclohexen-1-one and 3-iodo-2-cyclopenten-1-one) in the presence of Zn and catalytic amount of NiBr<sub>2</sub> to afford the corresponding homo 1,4-addition products in good yields. For 2,3dimethyl-1,3-butadiene, only the products RCH<sub>2</sub>C(CH<sub>3</sub>)=C(CH<sub>3</sub>)CH<sub>2</sub>R with Z geometry were observed. For cyclic dienes, the products observed are RCHCH=CHCHR(CH<sub>2</sub>)<sub>n</sub>CH<sub>2</sub> in which the two alkenyl substituents R are cis to each other. © 1998 Elsevier Science Ltd. All rights reserved.

## INTRODUCTION

Regio- and stereoselective addition to conjugated dienes mediated by transition metal complexes is useful in organic synthesis and has caused great attention in recent years. Known examples in this area include 1,4-diacetoxylation,<sup>1</sup> 1,4-acetoxychlorination (eq 1),<sup>2</sup> 1,4-hydrosilylation<sup>3-5</sup> and 1,4-carbosilylation.<sup>6</sup> In most cases, the reactions employed palladium complexes and to a less extent nickel complexes as catalysts and involved addition of both heteroatom nucleophiles<sup>7-10</sup> or one heteroatom and one carbon nucleophiles<sup>11-15</sup> to the conjugated dienes. The stereochemistry of these additions is of great interest. For cyclic dienes, both cis and trans 1,4-addition products may be obtained depending on the nucleophiles and on the reaction conditions.

The addition of two carbon units to conjugated dienes leading simultaneously to the formation of two carbon-carbon bonds is potentially an invaluable synthetic method. However, only a couple of reports concerning this type of addition were revealed. Takahashi *et al* described the first example of a palladium-catalyzed three-component coupling reaction including an aryl halide, stabilized carbon anion and 1,3-butadiene to achieve 1,4-arylation/alkylation of the diene (eq 2).<sup>16</sup> A related example is arylation/alkylation of nonconjugated dienes catalyzed by palladium complexes reported by R. C. Larock and his coworkers (eq 3).<sup>17</sup>



X, Y = COR,  $CO_2R$ , CN

In this paper, we describe an unusual nickel-catalyzed reaction of conjugated dienes with  $\beta$ -iodoenones or  $\beta$ -iodoenesters in the presence of zinc powder<sup>18</sup> leading to homo 1,4-dialkenylation of the dienes. The addition is highly regio- and stereoselective. In addition, the reaction pathway that results in the observed stereoselectivity appears to be different from that of the palladium-catalyzed 1,4-diacetoxylation<sup>1</sup> and 1,4acetoxychlorination.<sup>2</sup>

## **RESULTS AND DISCUSSION**

Treatment of 2,3-dimethyl-1,3-butadiene with  $\beta$ -iodocyclohexenone 1a in the presence of zinc powder and catalytic amount of nickel bromide and triphenylphosphine at 80 °C led to the isolation of 2a in 82 % yield. This product results from homo 1,4-addition of two 3-oxo-1-cyclohexenyl groups to the diene. Other cyclic  $\beta$ iodoenones 1b and 1c also react with 2,3-dimethyl-1,3-butadiene to give the corresponding homo 1,4-addition products 2b and 2c, respectively (eq 4 and Table I). Compounds 2a-c were produced with complete cis/trans

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selectivity. Only one single isomer was observed in each reaction, but it is difficult to assign the correct geometry for these products. The NOE experiment is not useful in determining the geometry, due to the highly symmetric nature of these products. The geometry of these products was assigned to be the same as that of compound 3 which was synthesized in a 12 % from a competing reaction of  $\beta$ -iodocyclohexenone and iodobenzene in 1:10 ratio with 2,3-dimethyl-1,3-butadiene. The major product in this reaction was 2a in 50 % yield. 3 was determined by NOE experiments to possess a cis structure.

β-Iodoenone	1,3-Diene	PPh3 <sup>b</sup>	Product	Yield(%) <sup>c</sup>	
	Ж	1	ᢅᡃ᠆᠆ᠿ	(2a)	82
	$\succ$	1	ᢅᡔ᠆ᠽ		21 <sup>d</sup>
	$\bigcirc$	0	$\circ \circ \circ \circ \circ$	(5)	80
	$\bigcirc$	0	òoó	(6)	90
	₩	1	ڮٮڒڔ۠	( <b>2b</b> )	85
	$\succ$	1	ᡷ᠆᠂ᠿ		34 <sup>d</sup>
	$\bigcirc$	0	<i>ڳ</i> ۞ڴ	(7)	45
	$\bigcirc$	0	\$-O-¢	(8)	82
	Ж	1	⁰ℊୢ୵୕ୣ୵ଡ଼°	(2c)	41 <sup>e</sup>
	$\succ$	1	⁰ु∽≻≺∠ु°	(2c)	75 <sup>¢ f</sup>

Table I. Nickel-Catalyzed 1,4-Dialkenylation of Conjugated Dienes<sup>a</sup>

<sup>a</sup> Unless otherwise noted all reactions were carried out at 80 °C in acetonitrile.<sup>b</sup> Equivalent relative to NiBr<sub>2</sub>. <sup>c</sup> Isolated yield. <sup>d</sup> A mixture of cis and trans isomer of the 1,4-addition product and 1,2-addition product were observed. *e* Side product **4** was formed in 12% yield. <sup>f</sup> The reaction was carried out in DMF.

For the reaction of 1c with 2,3-dimethyl-1,3-butadiene in acetonitrile, a spiro compound 4 was also isolated in 12 % yield. No such product was observed, if the reaction was carried out in DMF (Table I). A control reaction shows that 2c was completely converted to 4, if 2 was heated at 60 °C in acetonitrile in the presence of triethylamine for 12 h. The unusual structure of 4 was assigned based on the spectral properties. In the <sup>1</sup>H NMR spectrum, characteristic resonances for the two methyl, methine and vinyl protons appear at 1.38, 1.68, 3.34 and 5.94 ppm respectively. In agreement with the proposed structure, the <sup>13</sup>C NMR spectrum and

the results of DEPT experiments reveal the presence of two carbonyl and four vinyl carbons in addition to one sp<sup>3</sup> quaternary, six methylene and two methyl carbons.



In the presence of ZnBr<sub>2</sub> and Zn powder,  $\beta$ -iodoenones also react with conjugated cyclic dienes to give the corresponding homo 1,4-addition products (Table I). Thus, treating **1a** with 1,3-cycloheptadiene and 1,3cyclooctadiene led to the isolation of **5** and **6** in excellent yields (Table I). Similarly, **1b** undergoes homo 1,4-addition to 1,3-cyclohexadiene and 1,3-cycloheptadiene to give **7** and **8**, respectively. The regiochemistry of products **5** -**8** is revealed by the NMR data of these compounds. Key evidence for homo 1,4-addition instead of 1,2-addition is indicated by the observed single NMR resonances for the olefin protons and tertiary protons on the ring of the diene fragment in each product. The number of <sup>13</sup>C NMR resonances for each product also fully supports the presence of either a C<sub>2</sub> or plane symmetry excluding the possibility of a homo 1,2-addition reaction.

Unlike the results of cyclic  $\beta$ -iodoenones, *cis*- $\beta$ -iodoacrylates react with cyclic dienes to yield both 1,4and 1,2-addition products The ratio of 1,4- to 1,2-addition products and the total yield of each reaction are listed in eq 6. In all these cases, the 1,4-addition products are the major species and the acrylate groups in each product retain the cis geometry as indicated by the observed coupling constant of ~12 Hz between the two olefin protons.



The stereochemistry of homo dialkenylation of cyclic dienes is interesting. The coupling constant of 5.8 Hz between the allylic proton H-4 and the methylene protons at carbon-5 on the 6-member ring of product 7 appears to support a cis geometry for this product. For comparison, *cis*-1,4-dimethyl-2-cyclohexene reported by Bäckvall *et al.* exhibits a coupling constant of 5.5 Hz for the corresponding allylic and methylene protons.<sup>19</sup> The cis structure is unequivocally established by analysis of the H<sup>1</sup> NMR pattern of product 9 from 1,4-addition of methyl *cis*- $\beta$ -iodoacrylate to 1,3-cycloheptadiene. For a cis geometry, the methylene protons at carbon-6 are magnetically nonequivalent. On the other hand, due to the presence of a C<sub>2</sub> axis, a trans structure should results in equivalency of the two methylene protons at carbon-6. Although the <sup>1</sup>H NMR spectrum of 9 is complicate, the assignment of each signal can be achieved via decoupling techniques. The signal corresponding to the methylene protons clearly appears as an AB type pattern at 2.01 ppm after irradiating the signal at either

1.39 or 1.71 ppm for the two methylene protons at carbon-5 (or -7). This observation reveals nonequivalency of the two protons and establishes a cis geometry of the homo 1,4-addition products of cyclic dienes.

Effect of Reaction Conditions. The observed homo 1,4-addition reaction is extremely sensitive to the solvent, the concentration of the diene and ratio of phosphine to nickel. Table II summarizes the results of the effects of reaction conditions on the yields of product 2a. As shown in run (6 - 11), high yield of the addition product 2a was observed, if the reaction of 2,3-dimethyl-1,3-butadiene with 1a was carried out in acetonitrile, DMF or toluene. On the other hand, only the dehalogenation product of 1a was observed in THF (run 3 -4) and substitution of halide of 1a by MeO<sup>-</sup> was detected in methanol (run 12). The addition product but the reductive coupling product of 1a in 62 % yield was observed (run 5). As the concentration of diene increased to 6 M, 2a became the major product with a yield of 82 % (run 7). In the absence of PPh<sub>3</sub>, nickel bromide alone catalyzed the 1,4-addition reaction in acetonitrile, but the presence of 1 to 2 equivalents of this

Entry		Solvent	Catalyst	Temp	Product	Yield
			100 H I I	(°C)		(%)
1	1 <b>M</b>	THF	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	60	$\widetilde{\mathbf{D}} \rightarrow \widetilde{\mathbf{C}}$	-
2	6 M	THF	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	60	2a	43
3	1 M	THF	NiBr <sub>2</sub> /PPh3	60	<o< td=""><td>62</td></o<>	62
4	6M	THF	NiBr <sub>2</sub> /PPh <sub>3</sub>	60	<b>○</b> =0	41
5	1 <b>M</b>	CH <sub>3</sub> CN	NiBr2/PPh3	80	$\sim$	-
6	6 M	CH <sub>3</sub> CN	NiBr <sub>2</sub>	80	2a	80
7	6 M	CH <sub>3</sub> CN	NiBr <sub>2</sub> /PPh <sub>3</sub>	80	2a	82
8	6 M	CH <sub>3</sub> CN	NiBr <sub>2</sub> /2PPh <sub>3</sub>	80	2a	80
9	6 M	CH <sub>3</sub> CN	NiBr <sub>2</sub> /PPh <sub>3</sub>	80	2a	25
10	6 M	DMF	NiBr <sub>2</sub> /PPh <sub>3</sub>	80	2a	75
11	6 M	Toluene	NiBr <sub>2</sub> /PPh <sub>3</sub>	80	2a	76
12	6 M	MeOH	NiBr2/PPh3	80	MeO	100
					<=₀	
13	6 M	CH <sub>3</sub> CN/ H <sub>2</sub> O(1 eq)	NiBr <sub>2</sub> /PPh <sub>3</sub>	80	2a	70

**Table II.** Effects of Reaction Conditions on the Yields of the 1,4-Addition Product 2a.

<sup>&</sup>lt;sup>a</sup>All reactions were carried out under the following reaction conditions:  $\beta$ -iodocyclohexenone, 1.00 mmol; 2,3dimethyl-1,3-butadiene, as indicated in the Table; NiBr<sub>2</sub>, 0.100 mmol; Zn, 1.25 mmol and solvent, 0.50 mL; reaction time, 2 h at 80 °C and 4 h at 60 °C.

ligand appears to stabilize the nickel catalyst preventing it from rapid decomposition to nickel metal, particularly, near the end of the reaction. However, higher ratio of PPh<sub>3</sub> to nickel led to inhibition of the catalytic reaction and decreased of the yield of the 1,4-addition product (run 9).

**Mechanism.** The reaction pathway for the present catalysis is intriguing in view of the fact that two organic groups from  $\beta$ -iodoenones or  $\beta$ -iodoacrylate add successfully to the diene substrates. Based on the established nickel chemistry<sup>20</sup> and the observations shown below, a mechanism shown in Scheme 1 is proposed to account for the catalytic 1,4-addition reaction. The mechanism includes two separate pathways to achieve the addition. One involves slow metallation of  $\beta$ -iodoenone to give the corresponding zinc reagent, the other is a catalytic cycle. The first step in the catalytic cycle is the reduction of Ni(II) to Ni(0) by zinc metal.<sup>21</sup> This is followed by oxidative addition of 1a to the Ni(0) species. Coordination of the diene, insertion of the diene double bond into the nickel-carbon bond affords a  $\pi$ -allyl intermediate. Transmetallation between the nickel  $\pi$ -allyl species and the zinc reagent, 3-oxo-1-cyclohexen-1-ylzinc iodide, followed by reductive elimination gives the final 1,4-addition product and regenerated the Ni(0) species. The proposed slow metallation of  $\beta$ -iodoenone is confirmed by the observation that all  $\beta$ -iodoenones and  $\beta$ -iodoacrylates react slowly with zinc powder to yield the corresponding zinc reagents under the conditions for the catalytic homo 1,4-addition reactions.



An alternative pathway for the formation of the 1,4-addition product is from the reaction of nickel  $\pi$ -allyl intermediate with 1a as shown in eq 7. This pathway gains support from the known chemistry that Ni(II)-allyl species may act as a nucleophile reacting with aryl halides, vinyl halides and alkyl halides.<sup>22</sup>



To understand the nature of the present catalytic reaction and determine the correct pathways, several control experiments were carried out. Treatment of  $\beta$ -iodocyclohexenone with Ni(PPh<sub>3</sub>)<sub>4</sub> led to a rapid oxidative-addition reaction, but attempts to isolate the oxidative addition product led to decomposition of the nickel complex and the formation of the reductive dimerization product. The oxidative addition product, however, can be trapped readily by 2,3-dimethyl-1,3-butadiene to give, presumably, a  $\pi$ -allyl nickel intermediate. The latter is difficult to characterize by <sup>1</sup>H NMR spectroscopy resulting in the observation of non-informative broad signal (*vide infra*). Importantly, heating this  $\pi$ -allyl nickel intermediate with  $\beta$ -iodocyclohexenone did not yield the expected homo 1,4-addition product (eq 7), but treatment of this nickel  $\pi$ -allyl with 3-oxo-1-cyclohexen-1-ylzinc iodide (or  $\beta$ -iodocyclohexenone and zinc powder at 80 °C) led to the formation of 1,4-addition product **2a** in essentially quantitative yield. The above observations strongly support that, in the present catalytic reactions, the nickel  $\pi$ -allyl intermediates act an electrophile reacting with the zinc reagent generated *in situ* from the slow reaction of zinc metal with the alkenyl iodide in the solution. The alternative pathway (eq 7) with the nickel  $\pi$ -allyl intermediate behaving as a nucleophile to react directly with the alkenyl iodide giving the homo 1,4-addition product may be ruled out based on the observations.

Based on the mechanism shown in Scheme 1, we should be able to prepare 1,4-addition product 2a from 2,3-dimethyl-1,3-butadiene, 1a and the corresponding zinc reagent of 1a. However, mixing these three reagent and a catalytic amount of NiBr<sub>2</sub>/PPh<sub>3</sub> in acetonitrile, followed by heating at 80 °C gave the reductive dimerization product of 1a as the major product. The 1,4-addition product 2a was detected, but in less than 10 % yield. The yield of 2a was greatly improved to 40 %, if the zinc reagent of 1a was syringed into the catalytic solution slowly and continuously in a 4 h interval. Thus, it is important that the formation of zinc reagent is slow in the present catalysis to achieve high yield of the 1,4-addition product. If the rate of the formation of zinc reagent is faster than the insertion of diene into nickel-carbon bond, reductive dimerization becomes the major product.

It is noteworthy that treatment of chlorobenzene with Ni(PPh<sub>3</sub>)<sub>4</sub> yields a stable oxidative addition product Ni(PPh<sub>3</sub>)<sub>2</sub>(Ph)Cl,<sup>23</sup> although the reaction of  $\beta$ -iodocyclohexenone with Ni(PPh<sub>3</sub>)<sub>4</sub> does not give stable oxidative addition product. Ni(PPh<sub>3</sub>)<sub>2</sub>(Ph)Cl undergoes insertion reaction with 2,3-dimethyl-1,3-butadiene to yield a  $\pi$ -allyl species 12 which reveals in the <sup>1</sup>H NMR spectrum characteristic signals at  $\delta$  1.26 and 2.11 for the two methyl groups, at  $\delta$  3.07 (d, J = 15 Hz) and 3.38 (d, J = 15 Hz) for the methylene protons connected to the phenyl ring, at  $\delta$  2.17 and 2.22 for the two protons on the terminal carbon of the allyl group in addition to the signals in the aromatic region. Based on the intensity ratio of these <sup>1</sup>H NMR resonances, the structure of 12 is proposed as shown below. Treatment of this nickel  $\pi$ -allyl species afforded hetero 1,4-addition product 3 in quantitative yield at room temperature. In contrast, 12 does not react with  $\beta$ -iodocyclohexenone to give 3 at the temperature range 25 ~ 80 C. The results further confirm the reaction pathway in Scheme 1 with the  $\pi$ -allyl intermediate acting as an electrophile.



The observed cis stereochemistry of the 1,4-addition products of cyclic dienes also may be rationalized based on the mechanism shown in Scheme 1. By switching 2,3-dimethyl-1,3-butadiene to a cyclic conjugated diene, the insertion of diene into the nickel-carbon bond is expected to afford a cyclic  $\pi$ -allyl nickel(II) in which the organic substituent R is cis to the nickel center. The other key steps that determine the final stereochemistry of the addition product are the transmetallation between the zinc reagent and the cyclic  $\pi$ -allyl nickel(II) intermediate and the subsequent reductive elimination. It is known that zinc regents a RZnX reacts with  $\pi$ -allyl nickel(II) nickel(II) species via transmetallation instead of a direct nucleophilic attack at the  $\pi$ -allyl group.<sup>24</sup>

The mechanism for the present homo dialkenylation of cyclic dienes is apparently different from that of the palladium-catalyzed 1,4-diacetoxylation and 1,4-acetoxychlorination of cyclic dienes. To obtain a cis product in the palladium-catalyzed reactions, two trans attacks at the coordinated diene and  $\pi$ -allyl species are required. In the present nickel-catalyzed reactions, the observed cis products are due to two cis additions. Scheme 2 summarizes the key difference of these two reactions.



Based on the observation that 2c may be converted to the spiro compound 4, there is little doubt that 4 is from intramolecular cyclization of 2c. A mechanism involving deprotonation of a allylic proton in compound 2c followed by intramolecular Michael addition and protonation is proposed to account for the formation of 4 (Scheme 3).

In conclusion, we have demonstrated a regio- and stereoselective nickel-catalyzed homo dialkenylation of conjugated dienes. For 2,3-dimethyl-1,3-butadiene, only 1,4-addition products with Z geometry were observed, while for conjugated cyclic dienes, 1,4-addition products were the majors species. All the 1,4-addition products of cyclic dienes show a cis stereochemistry. A key step for the success of the present homo 1,4-addition is the slow metallation of  $\beta$ -iodoenones or enesters with zinc powder.

#### Scheme 3



### **EXPERIMENTAL SECTION**

<sup>1</sup>H and <sup>13</sup>C NMR experiments were performed on a Varian Gemini 300 or a Varian Unity 400 spectrometer. Infrared spectra were recorded on a Bomem MB-100 spectrophotometer while mass spectra was obtained on a Jeol JMS-D100 system. Microanalytical data were obtained on a Heraeus CHN-O-RAPID instrument.

Reagent chemicals were purchased from commercially available sources and used without further purification. All solvents were dried by standard methods and all reactions were performed under dry nitrogen atmosphere. 3-Iodo-2-cyclohexen-1-one,<sup>25</sup> 3-iodo-2-cyclopenten-1-one,<sup>25</sup> 5,5-dimethyl-3-iodo-2-cyclohexen-1-one,<sup>25</sup> ethyl (Z)-3-iodo-2-propenoate,<sup>26</sup> and 3-oxo-1-cyclohexen-1-ylzinc iodide<sup>27</sup> were prepared according to reported methods.

Synthesis of 2,3-Dimethyl-1,4-bis(3-oxo-1-cyclohexen-1-yl)-2-butene (2a). To a 50-mL sidearm flask were added NiBr<sub>2</sub> (0.100 mmol, 0.0204 g), PPh<sub>3</sub> (0.100 mmol, 0.0262 g) and Zn powder (1.25 mmol, 0.082 g). The system was purged by nitrogen three times. To the flask was then syringed acetonitrile (0.50 mL),  $\beta$ -iodocyclohexenone (1.00 mmol) and 2,3-dimethyl-1,3-butadiene (3.00 mmol) and the solution was stirred at 80 °C for 2 h. During the reaction, the solution turned from yellow to red color gradually. At the end of the reaction, the system was filtered through Celite. The filtrate was concentrated on a rotary evaporator and was separated on a silica gel column using a mixture of ethyl acetate and hexane as eluent to afford an oil product in 82 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.67 (s, 6 H), 1.99 (p, J = 6.4 Hz, 4 H), 2.24 (t, J = 6.4 Hz, 4 H), 2.36 (t, J = 6.4 Hz, 4 H), 2.90 (s, 4 H), 5.81 (s, 2 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 Hz, CDCl<sub>3</sub>):  $\delta$  18.85 (q), 27.81 (t), 34.56 (t), 38.14 (t), 48.26 (t), 124.7 (d), 168.3 (s), 199.9 (s). IR (neat): 2920, 2869, 1709, 1665, 1624, 1431, 1323, 1250, 1190, 1124, 967, 888, 757, 722 cm<sup>-1</sup>. HRMS : C<sub>18</sub>H<sub>24</sub>O<sub>2</sub>: calcd 272.1777, found 272.1791.

Compounds 2b, 2c and 4 were synthesized by following a similar procedure as that for 2a. Important spectral data are shown below and the yield of each product is listed in Table I.

**2,3-Dimethyl-1,4-bis(5,5-dimethyl-3-oxo-1-cyclohexen-1-yl)-2-butene** (2b). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.03 (s, 12 H), 1.67 (s, 6 H), 2.12 (s, 4 H), 2.22 (s, 4 H), 2.88 (s, 4 H), 5.84 (s, 2 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 Hz, CDCl<sub>3</sub>):  $\delta$  18.89 (q), 28.23 (q), 33.54 (s), 42.77 (t), 43.89 (t), 51.02 (t),

125.04 (d), 127.53 (s), 161.61 (s), 199.97 (s). IR (neat): 2955, 2871, 1711, 1664, 1460, 1417, 1369, 1274, 1151, 905, 735 cm<sup>-1</sup>. HRMS:  $C_{22}H_{32}O_2$ , calcd 328.2404; found 328.2409.

**2,3-Dimethyl-1,4-bis(3-oxo-1-cyclopenten-1-yl)-2-butene** (2c). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.70 (s, 6H), 2.39- 2.41 (m, 4H), 2.51- 2.53 (m, 4H), 3.07 (s, 4H), 5.88 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  19.16 (q), 31.39 (t), 35.44 (t), 38.71 (t), 127.44 (s), 130.39 (d), 180.44 (s), 209.65 (s). IR (neat): 2920, 1705, 1675, 1611, 1437, 1173, 840 cm<sup>-1</sup>. HRMS: C<sub>16</sub>H<sub>20</sub>O<sub>2</sub>, calcd 244.1458; found 244.1452.

**7,8-Dimethyl-6-(3-oxo-1-cyclopentenyl)spiro[4,4]non-7-en-2-one** (4). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.39 (s, 3 H), 1.68 (s, 3 H), 1.98-2.10 (m, 2 H), 2.12 (s, 2 H), 2.24-2.50 (m, 8 H), 3.34 (s, 1 H), 5.94 (s, 1 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 Hz, CDCl<sub>3</sub>):  $\delta$  12.99 (q), 13.90 (q), 30.16 (t), 35.29 (t), 36.72 (t), 38.24 (t), 47.61 (t), 48.98 (s), 50.04 (t), 63.27 (d), 130.82 (s), 132.07 (d), 132.98 (s), 182.35 (s), 209.36 (s), 217.92 (s).

Synthesis of 1,4-Bis(3-oxo-1-cyclohexen-1-yl)-2-cycloheptene (5). To a 50-mL sidearm flask were added NiBr<sub>2</sub> (0.100 mmol, 0.0204 g) and Zn powder (1.25 mmol, 0.082 g). The system was purged by nitrogen three times. To the flask was then syringed acetonitrile (0.50 mL),  $\beta$ -iodocyclohexenone (1.00 mmol) and 1,3-cycloheptadiene (3.00 mmol) and the solution was stirred at 80 °C for 2 h. The system was filtered through Celite. The filtrate was concentrated on a rotary evaporator and was separated on a silica gel column using a mixture of ethyl acetate and hexane as eluent to afford the desired pure product in 80 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.48-1.58 (m, 2 H), 1.64-1.78 (m, 4 H), 2.02 (m, 4 H), 2.37 (m, 8 H), 3.10 (d, J = 10.2 Hz, 2 H), 5.67 (s, 2 H), 5.92 (s, 2 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 Hz, CDCl<sub>3</sub>):  $\delta$  22.95 (t), 27.97 (t), 29.58 (t), 31.43 (t), 37.44 (t), 48.04 (d), 125.01 (d), 134.11 (d), 169.05 (s), 200.12 (s). IR (neat). (3420), 2937, 2861, 1714, 1660, 1348, 1259, 1191, 1086, 1028, 968, 888, 801 cm<sup>-1</sup>. HRMS : C<sub>19</sub>H<sub>24</sub>O<sub>2</sub>. calcd 284.1778, found 284.1782.

By following a similar procedure as that for 5, compounds 6 - 8 were synthesized. Important spectral data of these products are reported below.

**1,4-Bis(3-oxo-1-cyclohexen-1-yl)-2-cyclooctene** (6). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.45-1.59 (m, 4 H), 1.60-1.81 (m, 4 H), 2.00 (p, J = 6.2 Hz, 4 H), 2.33-2.42 (m, 8 H), 3.27 (t, 2 H), 5.53 (m, 2 H), 5.94 (s, 2 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 Hz, CDCl<sub>3</sub>):  $\delta$  22.76 (t), 25.57 (t), 28.81 (t), 33.80 (t), 37.41 (t), 44.73 (t), 124.61 (d), 131.09 (d), 168.24 (s), 199.86 (s). IR (neat). 2928, 1713, 1662, 1458, 1409, 1367, 1277, 1146, 903 cm<sup>-1</sup>. HRMS: C<sub>20</sub>H<sub>26</sub>O<sub>2</sub>, calcd 298.1934, found 298.1927.

**1,4-Bis(5,5-dimethyl-3-oxo-1-cyclohexen-1-yl)-2-cyclohexene** (7). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.03 (s, 6 H), 1.06 (s, 6 H), 1.56-1.63 (m, 2 H), 1.75-1.85 (m, 2 H), 2.19 (s, 2 H), 2.21 (s, 2 H), 2.24 (s, 4 H), 2.55 (t, J = 5.8 Hz, 2 H), 5.76 (s, 2 H), 5.91 (s, 2 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 Hz, CDCl<sub>3</sub>):  $\delta$  24.26 (t), 27.72 (q), 28.61 (q), 33.75 (s), 42.57 (d), 42.65 (t), 51.19 (t), 125.44 (d), 129.39 (d), 165.20 (s), 199.93 (s). IR (neat): 2951, 2870, 1709, 1659, 1464, 1366, 1303, 1279, 1143, 902 cm<sup>-1</sup>. HRMS: C<sub>22</sub>H<sub>30</sub>O<sub>2</sub>, calcd 326.2247; found 326.2258.

**1,4-Bis(5,5-dimethyl-3-oxo-1-cyclohexen-1-yl)-2-cycloheptene** (8). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.06 (s, 12 H), 1.51-1.54 (m, 2 H), 1.70-1.79 (m, 2 H), 2.08-2.21 (m, 2 H), 2.24 (s, 8 H), 3.09 (d, J = 10.4 Hz, 2H), 5.65 (s, 2 H), 5.93 (s, 2 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 Hz, CDCl<sub>3</sub>):  $\delta$  27.83 (q), 28.37 (q), 29.70 (t), 31.23 (t), 33.63 (s), 42.13 (t), 47.87 (d), 51.09 (t), 123.9 (d), 133.8 (d), 166.5 (s), 200.4 (s). IR

(neat): 2950, 2872, 1717, 1659, 1460, 1360, 1202, 1258, 1148, 904, 735, 699 cm<sup>-1</sup>. HRMS:  $C_{23}H_{32}O_2$ , calcd 340.2404; found 340.2416.

Synthesis of *cis*-1,4-Bis[(*Z*)-2-(methoxycarbonyl)-1-ethenyl]-2-cycloheptene (9). To a 25-mL sidearm flask were added NiBr<sub>2</sub> (0.050 mmol, 0.0109 g), PPh<sub>3</sub> (0.050 mmol, 0.0131 g) and Zn powder (1.25 mmol, 0.082 g). The system was purged by nitrogen three times. To the flask was then syringed methyl (*Z*)-3-iodopropenoate (1.00 mmol) and 1,3-cycloheptadiene .0.2 mL and the solution was stirred at 80  $\circ$  for 2 h. The solution changed color yellow to red gradually. At the end of the reaction, the system was cooled to room temperature and then filtered through Celite. The filtrate was concentrated on a rotary evaporator and was separated on a silica gel column using a mixture of ethyl acetate and hexane as eluent to afford the desired pure product in 24 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.39 (m, 2 H, CH<sub>2</sub>), 1.71 (m, 2 H, CH<sub>2</sub>), 1.93 (m, 1 H of CH<sub>2</sub>), 2.08 (m, 1 H of CH<sub>2</sub>), 3.74 (s, 6 H, OCH<sub>3</sub>), 4.26 (m, 2 H, CH), 5.50 (d, *J*=1.2 Hz, 2 H, =CH), 5.70 (dd, *J*=0.8, 12.0 Hz, 2 H, =CH), 6.22 (dd, *J*=10.1, 12.0 Hz, 2 H, =CH). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  29.63 (t), 33.67 (t), 39.62 (d), 51.10 (q), 117.71 (d), 134.81 (d), 154.00 (d), 166.42 (s). IR (neat): 2928, 2852, 1722, 1645, 1438, 1407, 1190, 999, 825 cm<sup>-1</sup>. HRMS: C<sub>15</sub>H<sub>20</sub>O<sub>4</sub>, calcd: 264.1356; found: 264.1369.

The following compounds 10,11 were synthesized by following a similar procedure as that for 9.

*cis*-1,4-Bis[(*Z*)-2-(ethoxycarbonyl)-1-ethenyl]-2-cycloheptene (10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.26 (t, *J*=6.9 Hz, 6 H, *CH*<sub>3</sub>), 1.36 (m, 2 H, *CH*<sub>2</sub>), 1.66 (m, 2 H, *CH*<sub>2</sub>), 1.92 (m, 1 H of *CH*<sub>2</sub>), 2.04 (m, 1 H of *CH*<sub>2</sub>), 4.12 (q, *J* = 6.9 Hz, 4 H, OC*H*<sub>2</sub>), 4.26 (m, 2 H, *CH*), 5.51 (d, *J*=1.6 Hz, 2 H, =*CH*), 5.69 (dd, *J*=1.0, 11.4 Hz, 2H, =*CH*), 6.21 (dd, *J*=10.0, 11.4 Hz, 2 H, =*CH*). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  14.22 (q), 29.64 (t), 33.64 (t), 33.59 (d), 59.90 (t), 118.19 (d), 134.83 (d), 153.54 (d), 166.01(s). IR (neat): 2981, 2923, 1717,1643, 1445, 1415, 1293, 1188, 1032, 827 cm<sup>-1</sup>. HRMS: C<sub>17</sub>H<sub>24</sub>O<sub>4</sub>, calcd: 292.1668; found: 292.1676.

*cis*-1,4-Bis[(*Z*)-2-(ethoxycarbonyl)-1-ethenyl]-2-cyclohexene (11). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.30 (t, *J*=7.0 Hz, 6 H, *CH*<sub>3</sub>), 1.54 (m, 2 H, *CH*<sub>2</sub>), 1.85 (m, 2 H, *CH*<sub>2</sub>), 4.10 (m, 2 H, *CH*), 4.18 (q, *J*=7.0 Hz, 4 H, OCH<sub>2</sub>), 5.65 (d, *J*=1.1 Hz, 2 H, =CH), 5.75 (d, *J*=11.0 Hz, 2H, =CH), 6.07 (dd, *J*=10.0, 11.0 Hz, 2 H, =CH). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  14.23 (q), 25.52 (t), 33.99 (d), 59.95 (t), 118.94 (d), 129.45 (d), 152.06 (d), 166.17(s). IR (neat): 2948, 1717, 1639, 1413, 1180, 1030, 952, 820 cm<sup>-1</sup>. HRMS: C<sub>16</sub>H<sub>22</sub>O<sub>4</sub>, calcd: 278.1512; found: 278.1519.

Synthesis of 2,3-Dimethyl-1-(3-oxo-1-cyclohexen-1-yl)-4-phenyl-2-butene (3). To a 25mL sidearm flask were added Ni(PPh<sub>3</sub>)<sub>2</sub>(Ph)Cl (0.100 mmol, 0.0695 g). The system was purged by nitrogen three times. To the flask was then syringed toluene (3.0 mL) and 2,3-dimethyl-1,3-butadiene (10 mmol, 0.82 g) and the solution was stirred at 60  $\circ$  for 2 h. The system was cooled to room temperature and to the solution was added a THF solution of 3-oxo-1-cyclohexen-1-ylzinc iodide (0.3 mmol, 1.0 mL, 0.3 M) with stirring. The color of the solution changed rapidly to deep brown. The solution was further stirred for 2 h at ambient temperature and then filtered through Celite. The filtrate was concentrated on a rotary evaporator and was separated on a silica gel column using a mixture of ethyl acetate and hexane as eluent to afford 3 in 87 % (0.0221g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.67(s, 3 H), 1.69 (s, 3 H), 1.99 (p, J = 6.2 Hz, 2 H), 2.24 (t, J = 6.2 Hz, 2 H), 2.38 (t, J=6.2 Hz, 2 H), 3.04 (s, 2 H), 3.38 (s, 2 H), 5.89 (s, 1 H), 7.13 (d, J = 7.2 Hz, 2 H), 7.18 (t, J =7.2 Hz, 1 H), 7.25 (t, J = 7.2 Hz, 2 H).  ${}^{13}C{1H}NMR$  (100 MHz, CDCl<sub>3</sub>):  $\delta$  18.64 (q), 18.86 (q), 22.81 (t), 29.79 (t), 37.38 (t), 39.98 (t), 42.83 (t), 125.03 (d), 125.21 (s), 125.92 (d), 127.50 (d), 128.33 (d), 130.91 (s), 140.06 (s), 161.98 (s), 199.99 (s). IR (neat): 2933, 1724, 1664, 1493, 1451, 1373, 1247, 1191, 966, 725, 699 cm<sup>-1</sup>. MS : 254, 196, 145, 91. HRMS: C<sub>18</sub>H<sub>22</sub>O, calcd 254.1672, found 254.1670.

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