

Review

**Stereoselective Transformation from Conjugated Alkynone to  
Nonconjugated (Z)- 3-Iodo-3-alken-1-one. Its Mechanism Study  
and Application in Organic Synthesis**

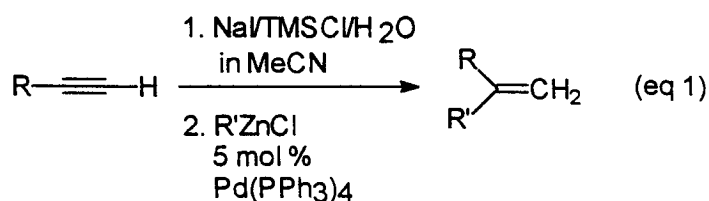
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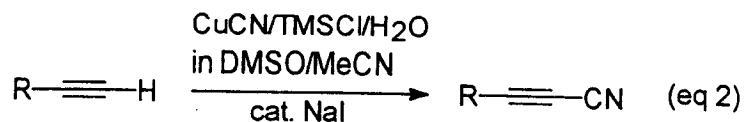
Treatment of conjugated alkynone with sodium iodide, chlorotrimethylsilane, and water in acetonitrile gave deconjugated (Z)-3-iodo-3-alken-1-one in good yield and with high stereoselectivity ( $\geq 95\%$ ). Mechanistic study showed that hydrogen iodide, generated from sodium iodide, chlorotrimethylsilane and water, underwent regioselective addition to the conjugated ynone, e.g. 3-decyn-2-one, to form conjugated (E)-4-iodo-3-decen-2-one and (Z)-4-iodo-3-decen-2-one. Then, chlorotrimethylsilane catalyzed the deconjugation reaction to form deconjugated (Z)-4-iodo-4-decen-2-one. The application of the above deconjugation reaction was demonstrated by the stereoselective synthesis of (Z)- $\alpha$ -alkylidene- $\gamma$ -butyrolactone, a plant growth regulator, and the palladium-catalyzed cross coupling reactions of (Z)-4-iodo-4-decen-2-one with organozinc chlorides.

INTRODUCTION

Recently, we have reported a one-pot conversion of terminal alkynes into *gem*-disubstituted alkenes by using *in situ* generated hydrogen iodide from NaI/TMSCl/H<sub>2</sub>O in MeCN and followed by the cross coupling with organozinc compounds in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (eq 1).<sup>1</sup> This method could provide a simple and useful method for the preparation of various *gem*-disubstituted-alkenes as a monomer for the preparation of polymers. We attempted to run hydrocyanation by using CuCN instead of NaI in MeCN. However, we only found that the terminal acetylene could transform into cyanoalkyne in good yield under CuCN/TMSCl/H<sub>2</sub>O and in the presence of catalytic amount of NaI in DMSO/MeCN (3:1) as shown in eq 2.<sup>2</sup>



R, R' = alkyl or aryl.



R = alkyl or aryl.

We then attempted to run hydroiodination on the conjugated ynone system in order to synthesize conjugated 3-iodo-2-alken-1-one, which was a useful type of substrate for cuprate reagent in running 1,4-addition and the following iodide elimination to form 3-substituted-2-alken-1-one.<sup>3</sup> However, we only isolated (*Z*)-3-iodo-3-alken-1-one in good yield and with high stereoselectivity ( $\geq 95\%$ ) as shown in eq 3.<sup>4</sup> Since the synthesis of stereoselective 3-halo-3-alken-1-ones is still a synthetic challenge. As to our knowledge, no other method could generate (*Z*)-3-iodo-3-alken-1-one with three useful functional groups in one-pot.<sup>5</sup> This method is becoming more useful since it could provide a simple way to form (*Z*)-3-iodo-3-alken-1-ol system after reduction with  $\text{NaBH}_4$  in MeOH.<sup>6</sup> Since, recently, Corey has demonstrated the synthetic utility of 2-haloallyl carbinols by a number of transformations.<sup>7</sup> Suzuki also reported the asymmetric synthesis of 2-bromohomoallylic alcohols and their application in organic synthesis of using tartrate ester of (2-bromoallyl)boronic acid.<sup>8</sup> Normant and his co-workers also used 2-iodohomoallylic alcohols in their metalla-Claisen rearrangement study to prepare stereoselective cyclopropane derivatives.<sup>9</sup> Furthermore, this one-pot reaction could generate three useful functional groups for further transformations.



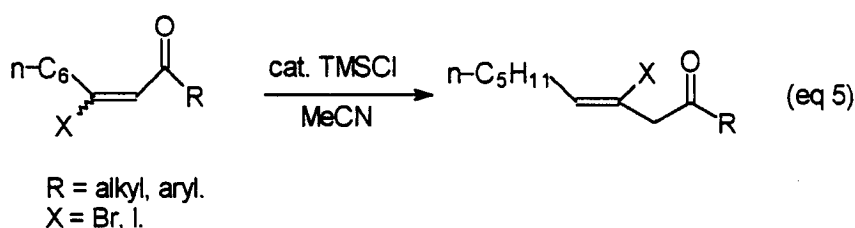
Attempted to form deconjugated propynoic acid derivatives under the similar reaction conditions only resulted the direct stereoselective hydroiodination products with (*Z*)-configuration in good yields as shown in eq 4.<sup>10</sup> Under the same reaction conditions, 5-phenyl-3-pentyn-2-one only gave direct stereoselective hydroiodination product, no deconjugation was observed.



## MECHANISM

When we treated 1 equiv of 3-decyn-2-one with anhydrous HI, generated *in situ* by the addition of 1 equiv of TMSCl to 1 equiv of NaI in 1 M solution of MeCN and followed by the addi-

tion of 0.5 equiv of H<sub>2</sub>O, (*E*)-4-iodo-3-decen-2-one and (*Z*)-4-iodo-3-decen-2-one<sup>11</sup> could be generated in 2-4 h and in 54% and 37% yields, respectively. Only trace amount (< 5%) of deconjugated (*Z*)-4-iodo-4-decen-2-one was detected by its crude <sup>1</sup>H-NMR spectral analysis. The products ratio did not change even prolonging the reaction time to 72 h. Without adding TMSCl in the reaction, only starting material was recovered. No great changes in the product yields were observed when we added 1 equiv of 1,4-benzoquinone prior to run the above reaction. Besides, using hexane instead of MeCN as the reaction solvent, no reaction was occurred. These results may rule out the possibility that the reaction involved a radical process. Water also played an important role in the reaction. In the absence of H<sub>2</sub>O, the starting material could be recovered in about 80% yield after 3 h at rt. Using excess of H<sub>2</sub>O (2 equiv), (*E*)-4-iodo-3-decen-2-one and (*Z*)-4-iodo-3-decen-2-one become the major products while (*Z*)-4-iodo-4-decen-2-one could be isolated only in trace amount (< 5%). However, when we used 1.1 equiv instead of 1 equiv of TMSCl to run the above reaction, (*Z*)-4-iodo-4-decen-2-one could be isolated in 76% yield in 4 h at rt along with only trace amount of (*E*)-4-iodo-3-decen-2-one and (*Z*)-4-iodo-3-decen-2-one as detected by <sup>1</sup>H-NMR spectral analysis. Thus, a little bit of excess TMSCl play an important role in this reaction. So, we can make our suggestion that (*E*)-4-iodo-3-decen-2-one and (*Z*)-4-iodo-3-decen-2-one were the real intermediates in the reaction and they were formed first through direct regioselective hydroiodination to the carbon-carbon triple bond. We also observed that TMSCl could be used as a catalyst to deconjugate β-bromo (or iodo) substituted α,β-unsaturated acyclic ketone to form the corresponding (*Z*)-β,γ-unsaturated ketones in good yields and with > 98% stereoselectivities as shown in eq 5.<sup>12</sup> The deconjugation process can be monitored by <sup>1</sup>H-NMR spectral analysis as shown in Fig. 1.



We also observed that while the reaction of (*E*)-4-iodo-3-decen-2-one with 1 equiv of TMSCl can be finished in 1 h, under the same concentration and conditions the corresponding (*Z*)-isomer can be deconjugated completely in 30 min. The <sup>1</sup>H-NMR spectra clearly showed that both isomers gave almost the same mixture of (*Z*)- and (*E*)-4-iodo-3-decen-2-one with a ratio of about 1 to 2 in 3 to 5 min. After prolonging the reaction time, both isomers were isomerized completely to the same product in 30 min to 1 h. We then proposed the mechanism for this deconjugation process as follows: TMSCl acts as a Lewis acid to activate both (*E*)- and (*Z*)-enone to form silyl enol ether allylic cation intermediates. This equilibrium of (*Z*)- and (*E*)-isomers can be reached very fast when TMSCl was regenerated. TMSCl can also act as a Lewis acid to activate both enones. At this stage, the chloride anion acts as a weak base to abstract one of the two allytic protons to form HCl and the silyl dienol ether intermediate. Since the allylic protons in the (*Z*)-isomer has less steric hindrance than that of the (*E*)-isomer, they are more easily to be accessed than that in the (*E*)-isomer by the chloride anion. Thus, the process of deconjugation for the (*Z*)-

isomer was faster than the (*E*)-isomer. Since the coexistence of HCl and the silyl dienol ether are inevitable and the following kinetic protonation<sup>13</sup> of the silyl dienol ether with HCl to form the deconjugated product and TMSCl is also very fast, we can not observe the expected silyl dienol ether intermediate by <sup>1</sup>H-NMR spectral analysis even at -40 °C. Since the chloride anion is a weak base so that only when *n*-pentyl group and the iodo substituent are on the *syn* position of the C-C single bond to allow the proton abstraction. The following double bond migration and protonation should give (*Z*)-configuration in the deconjugated product (**Scheme I**).

One may think that using either HCl or HI in catalytic or stoichiometric amount may undergo the same reaction process. However, we observed that none of them gave the same results as we used TMSCl in the above deconjugation reaction. Both 10 mol % of HCl (37% aq. solution) and HI (47% aq. solution) reacted with (*E*)-4-iodo-3-decen-2-one to give predominantly a mixture of C-C double bond isomerized and conjugated products (53-93%, *E/Z* = 2/1) after 48 h at

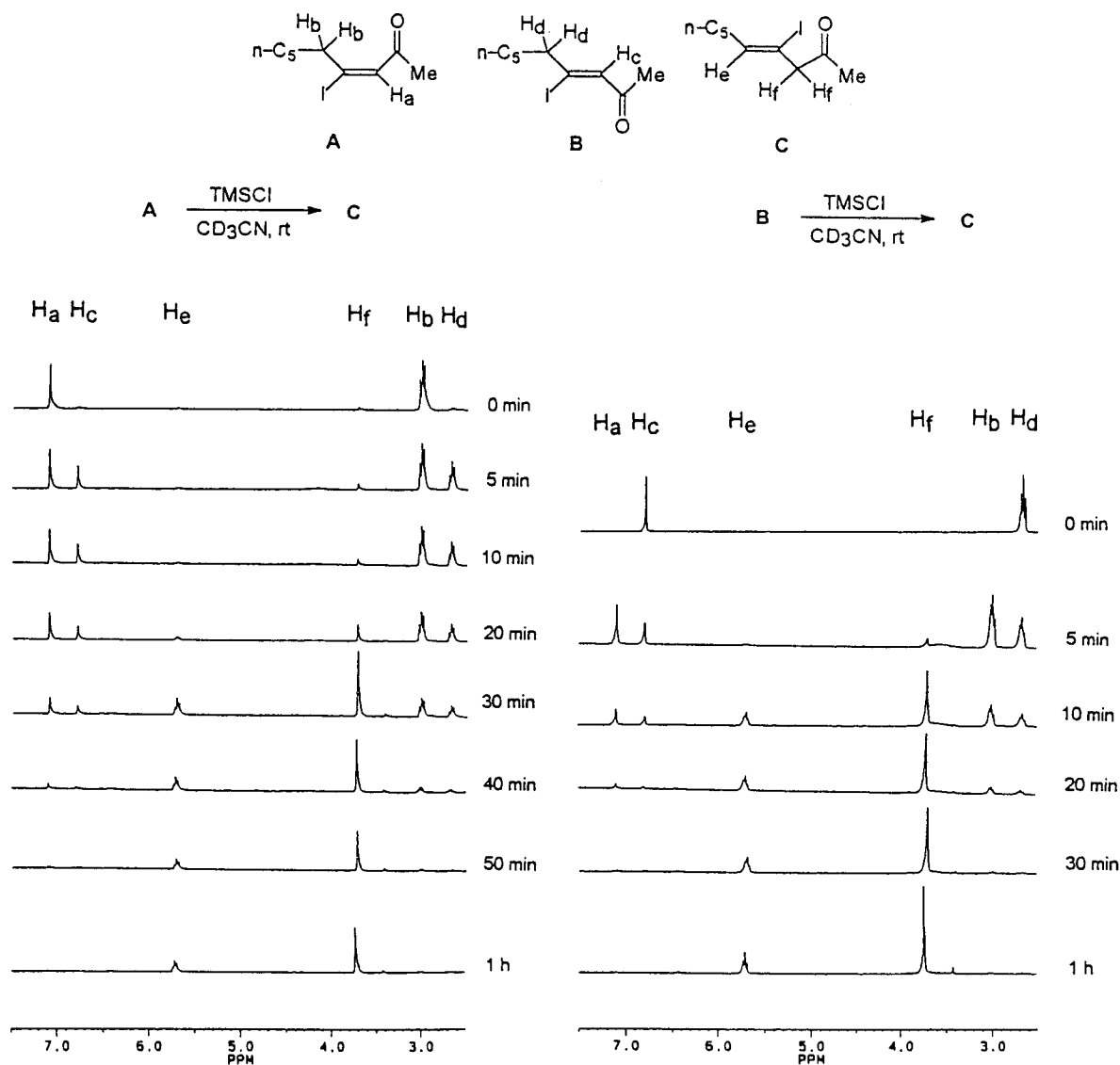
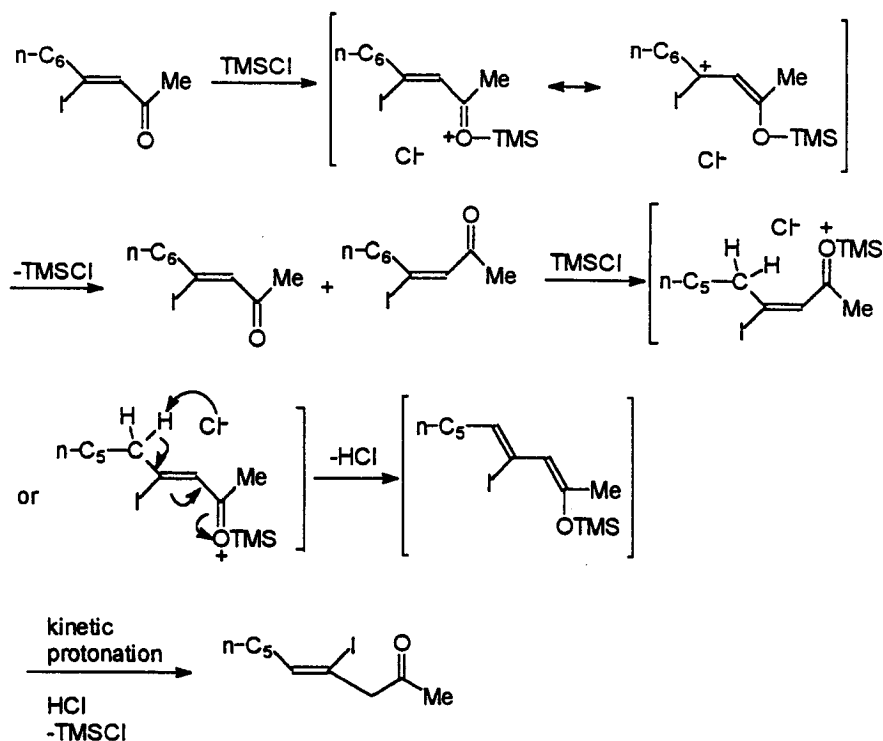


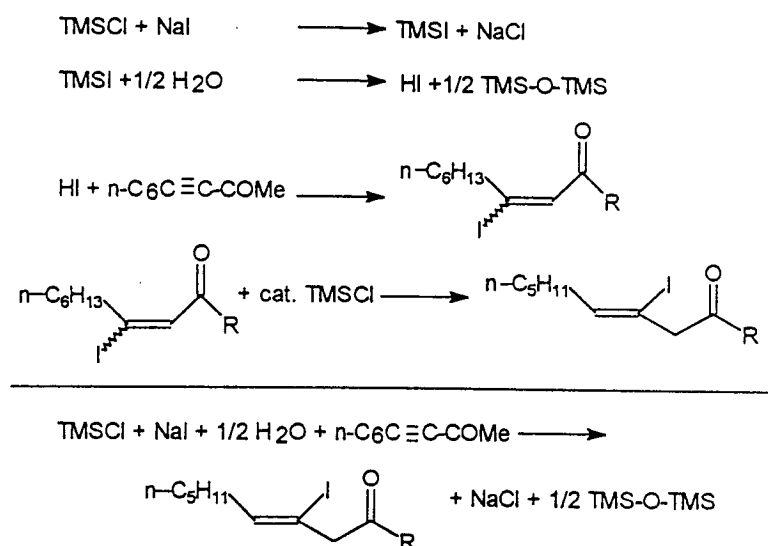
Fig. 1. <sup>1</sup>H-NMR Spectra Changes with Time for TMSCl-Promoted Deconjugation of (*E*)- and (*Z*)-4-Iodo-3-decen-2-one to Form (*Z*)-4-Iodo-4-decen-2-one

**Scheme I** Plausible Mechanism for the TMSCl-Catalyzed Deconjugation of (Z)-4-iodo-4-decen-2-one

rt. Used 1 equiv of HCl gave both (Z)-4-iodo- and (Z)-4-chloro-4-decen-2-one in 81% total yield with 1 to 1 ratio after 72 h at rt. While using 1 equiv of HI gave 7 to 1 ratio of (Z)- and (E)-4-iodo-4-decen-2-one with 77% total yield in both 9 and 96 h at rt.

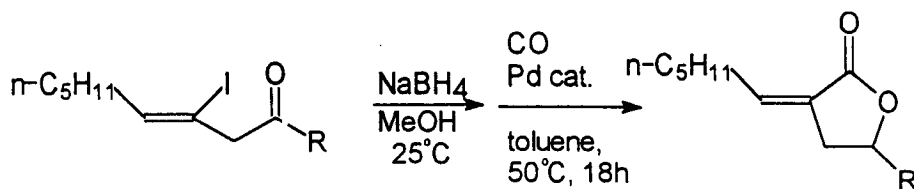
We attempted to do the deconjugation by treating (E)-4-iodo-3-decen-2-one or (Z)-4-iodo-3-decen-2-one with 1.1 equiv of TMSCl and 1 equiv of NaI and 0.5 equiv of H<sub>2</sub>O in MeCN. However, starting materials were recovered in 90% to 94% yields, respectively, and only trace amount of (Z)-4-iodo-4-decen-2-one was detected by <sup>1</sup>H-NMR spectral analysis. This result can be rationalized that once the oxygen of the carbonyl group was protonated first by the fast *in situ* generated HI, further coordination of the carbonyl group by TMS group was becoming difficult. So that, no further deconjugation process would be happened. When water was added in excess, the deconjugation process will be terminated. Since both TMSI and TMSCl will form HI and HCl very quickly when water was added in excess. The AM1 calculations from PC Spartan Plus program showed that the heat of formation for (E)-4-iodo-3-decen-2-one, (Z)-4-iodo-3-decen-2-one, and (Z)-4-iodo-4-decen-2-one were -48.19, -46.92, and -49.62 kcal/mol, respectively. Thus, the relative stability order is (Z)-4-iodo-4-decen-2-one > (E)-4-iodo-3-decen-2-one > (Z)-4-iodo-3-decen-2-one. This may also support that the deconjugation process may be dominated by the thermostability of the iodoenone isomers. Thus, we proposed the mechanism for this reaction as follows: TMSI was formed from NaI and TMSCl, HI was then formed in the presence of H<sub>2</sub>O, regioselective hydroiodination of conjugated 3-decyn-2-one would form conjugated (E)-4-iodo-3-decen-2-one and (Z)-4-iodo-3-decen-2-one. Then, TMSCl catalyzed the deconjugation to form deconjugated (Z)-4-iodo-4-decen-2-one (Scheme II).

**Scheme II** Plausible Hydroiodination and Deconjugation Processes for 3-Decyn-2-one



**APPLICATIONS IN ORGANIC SYNTHESIS**

Recently, the stereoselective synthesis of (*Z*)- $\alpha$ -alkylidene- $\gamma$ -butyrolactone has become attractive since these compounds can be used as a plant growth regulator,<sup>14</sup> or as an important intermediate to the synthesis of obtusilactone isolated from *Lindela obtusiloba*, a cytotoxic natural product.<sup>15</sup> Efficient methods for the preparation of lactones containing both saturated and unsaturated five or six-membered rings have been considerable interest for synthetic organic chemists in view of their recognized biological activities, for example, fungicidal, herbicidal, antibiotic, and antitumor properties.<sup>16</sup> Although several methods have been reported for the introduction of an alkylidene group at the  $\alpha$ -position of a  $\gamma$ -butyrolactone,<sup>17</sup> there is no general procedure being reported in the literature for the stereoselective synthesis of the exocyclic double bond with the (*Z*)-configuration. Usually, synthetic procedures to the  $\alpha$ -alkylidenelactones generally involve either (a) conversion of an existing group at the  $\alpha$ -position on a preformed lactone ring to the corresponding  $\alpha$ -methylene or  $\alpha$ -alkylidene group<sup>17</sup> or (b) formation of the  $\alpha$ -methylene- or  $\alpha$ -alkylidenelactone from acyclic precursors containing all of the desired functional groups *via* a ring closure reaction.<sup>18</sup> We have found that reduction of (*Z*)-3-iodo-3-alken-1-one with NaBH<sub>4</sub> in MeOH at rt gave (*Z*)-3-iodo-3-alken-1-ol in good yield (> 90 %) with no loss of stereochemistry as judged by <sup>1</sup>H NMR spectral analyses. In the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst, Et<sub>3</sub>N, and CO in toluene, intramolecular cyclization of (*Z*)-3-iodo-3-alken-1-ol afforded (*Z*)- $\alpha$ -alkylidene- $\gamma$ -butyrolactone with or without substituent at the  $\gamma$ -position in 18 h and in good yields as shown in Table I. The stereochemistry of the exocyclic double bond was determined by 2D NOESY (phase sensitive) <sup>1</sup>H NMR spectral analyses. A stoichiometric amount of tributyltin hydride was found to be a good reducing agent to replace triethylamine in the above reaction to shorten the reaction time to about 2.5 h. Similar reaction conditions have been reported in the formylation of organic halides.<sup>8,9</sup> The plausible mechanism of the reaction was shown in **Scheme III**. Thus, the oxidative addition of (*Z*)-3-iodo-3-alken-1-ol with palladium(0) catalyst to yield vinylpalladium(II) iodide

Table 1. Conversion of (*Z*)-3-iodo-3-alken-1-one into (*Z*)- $\alpha$ -alkylidene- $\gamma$ -butyrolactone

Entry	R =	Yield (%)
1	-H	67
2	-Me	62
3	-Et	63
4	-C <sub>5</sub> H <sub>11</sub> -n	68 <sup>a</sup>
5	-Ph	72
6		66
7		56

<sup>a</sup> Z/E ratio was 97/3 as determined by <sup>1</sup>H NMR spectral analysis.

complex, followed by the CO insertion into the palladium-carbon  $\sigma$  bond, and reductive elimination induced by the alcohol to afford (*Z*)- $\alpha$ -alkylidene- $\gamma$ -butyrolactone and regenerate the palladium(0) catalyst. It is worth noting that reports of the preparation of  $\alpha$ -alkylidenelactones with high stereoselectivity and in high yield are scarce.<sup>6</sup>

We then undertook the palladium-catalyzed cross coupling reactions of (*Z*)-4-iodo-4-decen-2-one with organozinc chlorides. The one-pot results obtained in the hydroiodination of 3-decyn-2-one followed by cross coupling with these organozinc chlorides are shown in Table 2. The

### Scheme III Plausible Mechanism for Pd-Catalyzed CO Insertion and Cyclization

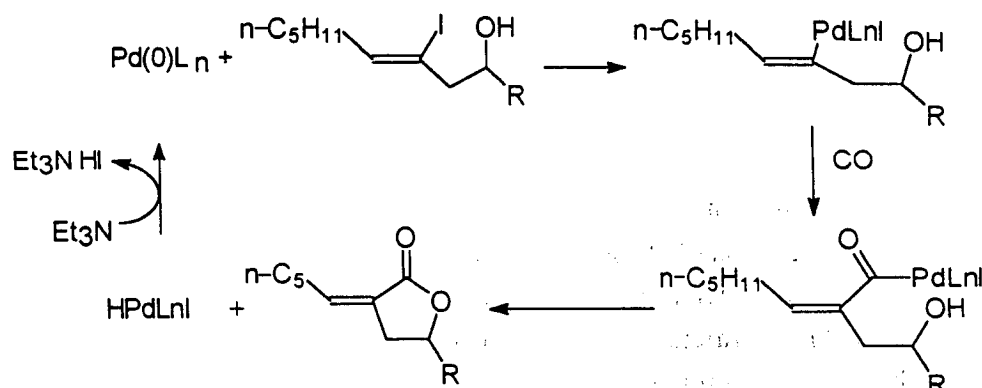
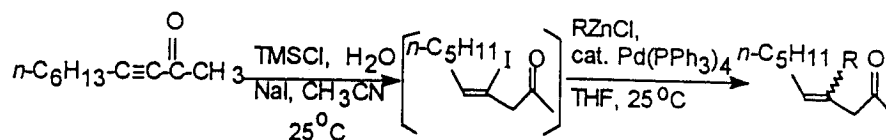


Table 2. One-Pot Conversion of 3-Decyn-2-one into 4-Substituted-4-decen-2-one



Entry	R	Yield, %	(Z):(E)
1	Me-	72	1:1
2	n-Bu-	67	1:1
3	Ph-	83	1:1
4		79	20:1
5	Ph-C≡C-	76	1:3
6	Me <sub>3</sub> SiC≡C-	74	1:1

yields of products from the cross coupling reaction are high but with low stereoselectivities. We observed that there was no change in the stereochemistry of the carbon-carbon double bond after the intermediate (*Z*)-4-iodo-4-decen-2-one was stirred with 5 mol % of Pd(PPh<sub>3</sub>)<sub>4</sub> in THF at rt for 12 h as judged by <sup>1</sup>H NMR spectral analysis. Once phenylzinc chloride was added to the reaction mixture, a 1:1 mixture of the *E* and *Z* stereoisomers of the product 4-phenyl-4-decen-2-one was formed after 0.5 h at rt as determined by <sup>1</sup>H NMR spectral analysis. This confirmed that the basic organozinc compound causes the loss in the stereoselectivity of the cross coupling step. This loss may result from coordination of the zinc cation with the carbonyl oxygen after transmetalation. This coordination effect will accelerate the β-elimination process to form an alleneone intermediate, as shown in Fig. 2. After non-stereoselective re-hydropalladation and reductive elimination, an (*E*)/(*Z*) mixture will be produced with low stereoselectivity. In the case of furylzinc chloride, we observed mainly retention of the stereochemistry of the carbon-carbon double bond in the cross coupling process. This result may be due to coordination of the oxygen atom in the furan ring with the zinc cation, which in the same way decreases the rate of the β-elimination relative to reductive elimination.<sup>19</sup>

## EXPERIMENTAL

### (*Z*) 4-Iodo-4-decen-2-one

Put 1.1 to 1.5 equiv of oven dry sodium iodide and a stirring bar into a round-bottom flask with one side arm. Seal the outlet of the side arm with double rubber septa and tighten it with copper wire. Connect the other outlet of the flask with an adapter with stopcock and tighten the two glasswares together with a stainless clamp. Connect the adapter to the high vacuum oil pump. Make sure to put high vacuum grease at the joints. Use either a high temperature heat gun or a



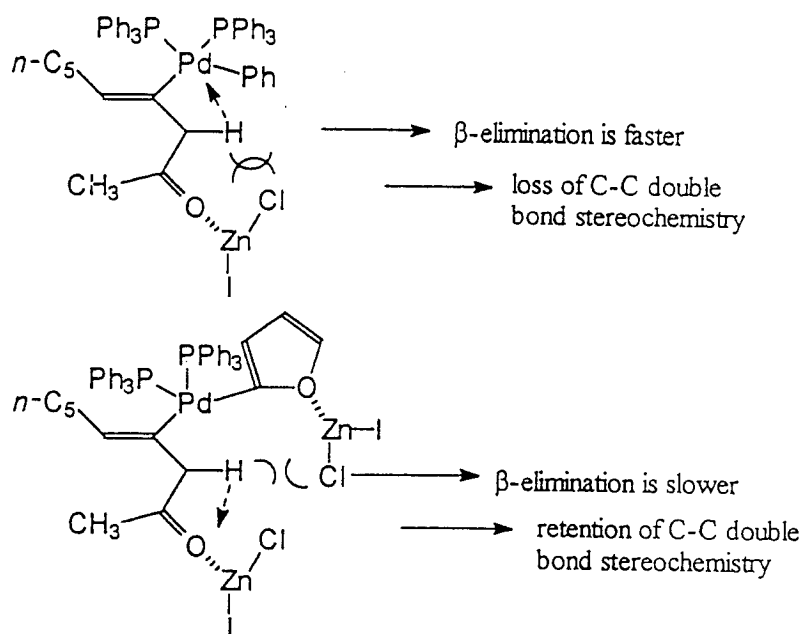


Fig. 2. Coordination Effects in the Pd-Catalyzed Cross Coupling Reaction

micro-torch to heat sodium iodide and the flask. One may heat sodium iodide until it melt without any bad results. *One should also remove the water condensed on the upper inner wall of the flask by heating it with heat gun or torch.* While the flask is cooled under the vacuum, close the stopcock and flush the flask with dry nitrogen with high purity. Use dry syringe to add dry acetonitrile into the flask and start stirring.<sup>20</sup> Use dry syringe to take 1.1 to 1.5 equiv of chlorotrimethylsilane and add it to the middle of the flask. Keep stirring for another 20 minutes at rt. Use dry syringe to take 0.5 equiv of water and add it into the middle of the flask. Keep stirring for another 10 minutes at rt. Use dry syringe to take 1 equiv of 3-decyn-2-one and add it quickly into the flask. There is no big difference to the reaction results if one add ynone dropwise or quickly. After stirring for another 4 h, the reaction mixture was quenched with saturated sodium thiosulfate and extracted with ether three times. The organic layer is dried over magnesium sulfate followed by filtration, concentration, and chromatography (silica gel, ethyl acetate/hexanes = 8/1) to give (*Z*)-4-iodo-4-decen-2-one as a colorless oil ( $R_f = 0.53$  on Si60 F254, ethyl acetate/hexanes = 4/1):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS)  $\delta$  0.90 (t,  $J = 7$  Hz, 3 H), 1.28-1.45 (m, 6 H), 2.14 (q with one singlet at  $\delta$  2.18,  $J = 7$  Hz, 5 H), 3.70 (s, 2 H), 5.67 (t,  $J = 7$  Hz, 1 H) ppm;  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , TMS)  $\delta$  13.93, 22.34, 27.71, 29.26, 31.18, 36.51, 59.08, 95.89, 140.75, 204.89 ppm; IR (neat) 2959 (m), 2930 (m), 1708 (s), 1630 (w), 1580 (w), 1455 (w), 1410 (w), 1353 (m), 1205 (m), 1150 (m)  $\text{cm}^{-1}$ ; MS  $m/z$  280 ( $\text{M}^+$ ) 209, 170, 153, 135, 109, 95, 81, 71, 67, 54; HRMS calcd for  $\text{C}_{10}\text{H}_{17}\text{IO}$  280.0325, found 280.0328; Anal. Calcd for  $\text{C}_{10}\text{H}_{17}\text{IO}$ : C, 42.87; H, 6.11. Found: C, 42.92; H, 6.13.

#### (*E*)-4-Iodo-3-decen-2-one

$^1\text{NMR}$  ( $\text{CDCl}_3$ , TMS)  $\delta$  0.90 (t,  $J = 7$  Hz, 3 H), 1.2 - 1.6 (m, 8 H), 2.15 (s, 3 H), 3.05 (t,  $J =$

7 Hz, 2 H), 7.02 (s, 1 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  14.00, 22.48, 28.08, 29.73, 31.15, 31.51, 41.53, 130.83, 138.52, 195.22 ppm; IR (neat) 1691 (s), 1577 (s), 1350 (m), 1109 (m), 906 (s), 713 (m)  $\text{cm}^{-1}$ ; MS  $m/z$  280 ( $\text{M}^+$ ), 153, 128, 111, 95.

#### (Z)-4-Iodo-3-decen-2-one

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.90 (t,  $J = 7$  Hz, 3 H), 1.2 - 1.6 (m, 8 H), 2.28 (s, 3 H), 2.67 (t,  $J = 7$  Hz, 2 H), 6.66 (s, 1 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  13.44, 22.48, 27.94, 29.32, 31.47 (2 C's), 48.02, 117.75, 131.22, 196.06 ppm; IR (neat) 1692 (s), 1587 (s), 1355 (m), 1108 (m), 906 (s), 745 (m)  $\text{cm}^{-1}$ ; MS  $m/z$  280 ( $\text{M}^+$ ), 153, 128, 111, 95; HRMS calcd for  $\text{C}_{10}\text{H}_{17}\text{IO}$  280.0325, found 280.0326.

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20. Normally, 1 mmol of NaI with 1 mL of MeCN to form about 1M solution is good enough to dissolve NaI completely. Make sure to completely dissolve NaI at this stage to do further steps.

從共軛炔基炔酮到非共軛(順式)-3-碘-3-炔基烯-1-酮  
的高立體選擇性轉變。其反應機構及  
在有機合成上的研究

羅芬臺

摘 要

共軛型的炔酮類化合物在碘化鈉，氯化三甲基矽及水，並以乙腈作溶劑下，可進行反應得到產率及立體選擇性均佳的非共軛型的(順式)-碘化烯酮類化合物。研究結果顯示 3-癸炔-2-酮的反應是由先產生的碘化氫進行炔基加成反應，得到(順式)-及(反式)-4-碘-3-癸烯-2-酮，再進行氯化三甲基矽催化的非共軛化反應產生(順式)-4-碘-4-癸烯-2-酮。利用上述非共軛化反應，我們成功地開發一種利用碘化非共軛烯酮的分子來合成在 $\alpha$ -位置上帶有順式的碳-碳雙鍵丁內酯化合物。此類化合物可用來調節植物生長的快慢。我們也利用鈀催化劑及有機鋅化合物對(順式)-4-碘-4-癸烯-2-酮進行耦合反應產生俱有三取代基的烯類化合物。