Nickel- and Zinc-Promoted [2 + 2 + 2] Cycloaddition of Diynes and α,β-Enones

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The [2 + 2 + 2] cycloaddition of diynes and enones occurred in the presence of both nickel and zinc together. This binary metal-mediated reaction had two interesting features: (1) a terminally unsubstituted diyne reacted with an enone to give an aromatic compound with the concomitant incorporation of two hydrogen atoms abstracted from an expected 1,3-diene product into another molecule of the starting enone and (2) a trimethylsilyl-substituted diyne reacted with an equimolar amount of enone to regioselectively afford a 1,3-diene, in which the trimethylsilyl group is adjacent to the carbonyl group.

Introduction

[2 + 2 + 2] cycloadditions of three unsaturated substrates lead to the formation of three new carbon−carbon bonds in one step.[1] Such reactions are generally promoted by the use of various transition-metal complexes as catalysts or stoichiometric reagents.[2] In particular, the partially intramolecular cycloadditions of diynes and alkynes result in the construction of chemo- and regioselective annelated benzenes (Chart 1).[3] Recently, the regioselective cycloaddition of differently substituted diynes with 1-alkynes was also reported.[4] On the contrary, the [2 + 2 + 2] cycloaddition of diynes and alkenes has not yet been established as a synthetic method, since two problems remain unsolved: i.e., (i) a high ratio of alkene to diyne is required[5] and (ii) there is no known example of regiochemical control for the reaction of a diyne with an alkene.[6,7]

We recently reported the cotrimerization of α,β-enones and alkynes in the presence of a nickel and aluminum catalytic system.[7] However, this binary catalytic system could not be applied to the reaction of diynes with enones. We have since researched other combinations of metals and have found an efficient system for this reaction.

Chart 1

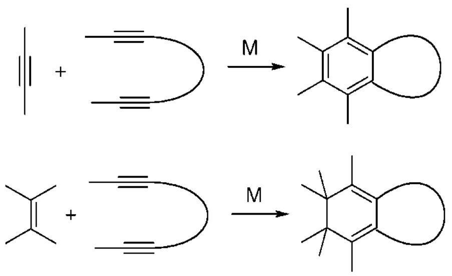
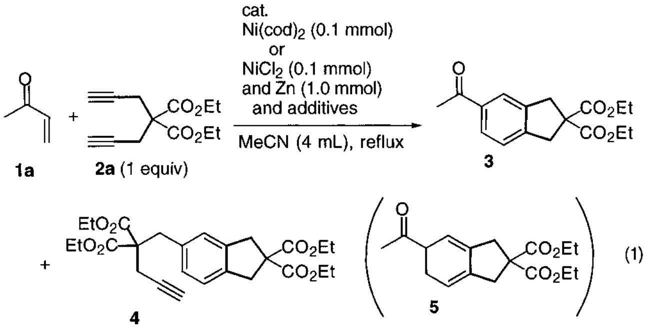


Table 1.



run	catalyst	$ZnCl_2$, equiv	Et_3N, equiv	**1a**, equiv	time, h	yield,[a] % **3/4**
1	$Ni(cod)_2$	0	0	2.1	2	(13)/trace
2	$NiCl_2$/Zn	0	0	2.1	2	21/0
3	$NiCl_2$/Zn	0.6	0	2.1	2	34/0
4	$NiCl_2$/Zn	1.4	0	2.1	2	44/0
5	$NiCl_2$/Zn	1.4	1.5	2.1	2	77/0
6	$Ni(cod)_2$	1.4	1.5	2.1	2	31/0
7	$NiCl_2$/Zn/COD[b]	1.4	1.5	2.1	2	29/0
8	$NiCl_2$/Zn	1.4	1.5	1.1	8	37/0

[a] Isolated yield. GC yield is in parentheses. [b] 1,5-Cyclooctadiene (COD, 20 mol %) was added under the reaction conditions in run 5.

Results and Discussion

When the reaction of 3-buten-2-one (**1a**) with a terminally unsubstituted diyne **2a** (1 mmol) was carried out in the presence of $Ni(cod)_2$ (10 mol %) in MeCN at reflux for 2 h, the starting material **2a** disappeared and a small amount of cycloadduct was obtained in 13% yield along with a trace amount of dimer **4** (run 1 in Table 1).[8,9] The cycloadduct was assigned to be an aromatic compound **3**, rather than the expected 1,3-cyclohexadiene **5**, based on the ^1H NMR spectra. The use of $NiCl_2$ (10 mol %) and Zn dust (100 mol %) instead of $Ni(cod)_2$ afforded the desired **3** in 21% isolated yield (run 2).[9] In this reaction, $NiCl_2$ would react with Zn to prepare a Ni(0) species along with $ZnCl_2$. The additional $ZnCl_2$ more effectively promoted the desired cycloaddition of **1a** and **2a** (runs 3 and 4).[9] When Et_3N was added to the reaction medium,

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(1) Dower, W. V.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1982**, *104*, 6878.

(2) (a) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (b) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49.

(3) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.

(4) McDonald, F. E.; Zhu, H. Y. H.; Holmquist, C. R. *J. Am. Chem. Soc.* **1995**, *117*, 6605.

(5) Recent reports: Grigg, R.; Scott, R.; Stevenson, P. *J. Chem. Soc., Perkin Tarns. 1* **1988**, 1365. Zhou, Z.; Battaglia, L. P.; Chiusoli, G. P.; Costa, M.; Nardelli, M.; Pelizzi, C.; Predieri, G. *J. Chem. Soc., Chem. Commun.* **1990**, 1632. Zhou, Z.; Costa, M.; Chiusoli, G. P. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1399.

(6) For the regioselective cycloaddition of completely intermolecular alkenes and alkynes, see: Chalk, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 5928. Balaich, G. J.; Rothwell, I. P. *J. Am. Chem. Soc.* **1993**, *115*, 1581.

(7) Ikeda, S.; Mori, N.; Sato, Y. *J. Am. Chem. Soc.* **1997**, *119*, 4779.

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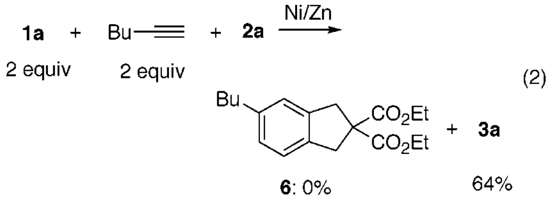
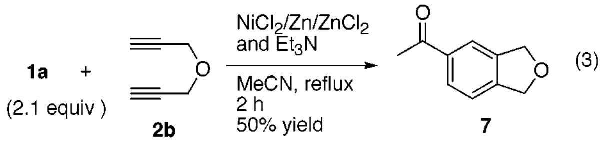
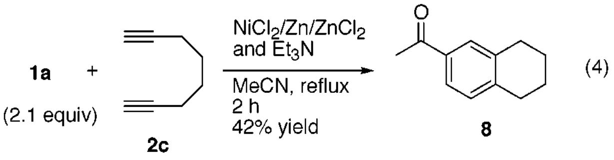
cycloaddition proceeded to afford **3** in 77% yield (run 5). The presence of 1,5-cyclooctadiene (COD) impaired the cycloaddition (runs 6 and 7). When **2a** was reacted with an equimolar amount of **1a** under the reaction conditions in run 5, **3** was obtained in only 37% yield (run 8).

The nickel and zinc system did not promote the cycloaddition of **2a** with 3-butyn-2-one. Moreover, in the crossover experiment depicted in eq 2, cycloadduct **6**, arising from the reaction of 1-hexyne with **2a**, was not obtained. These results indicate that **2** specifically reacted with **1** in the presence of this binary metal system.[10]

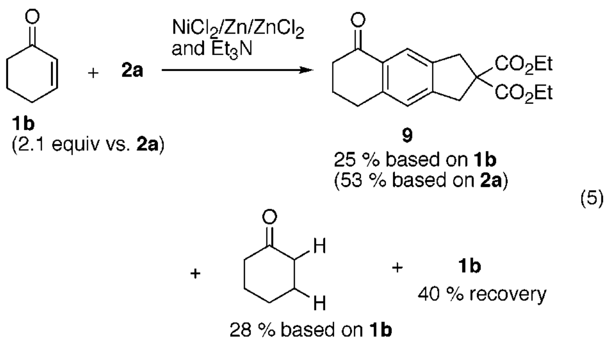


Diynes **2b** and **2c** also reacted with **1a** to give the corresponding aromatized cycloadducts **7** and **8**, respectively (eqs 3 and 4). The expected cyclohexadienes were not obtained in these reactions.

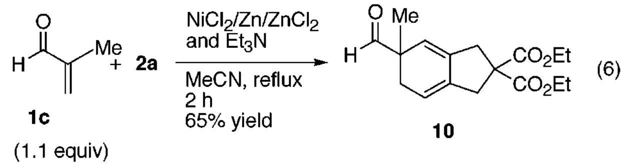




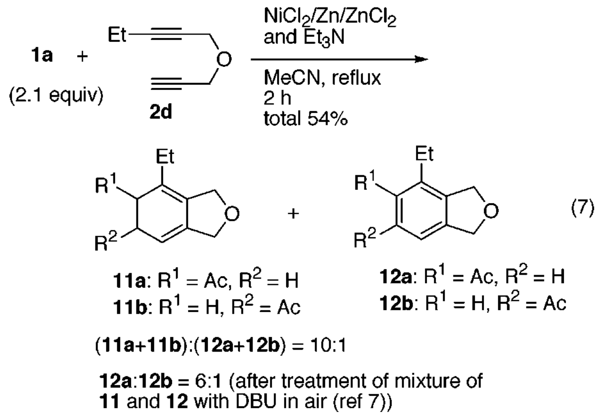
The stoichiometry of these reactions indicates that two hydrogen atoms in the reactants are formally abstracted from the expected product, i.e., 1,3-cyclohexadiene. Although the aromatization of the obtained products in situ is generally known to be a secondary reaction in the cycloaddition of alkynes with alkenes,[11] the details have not been fully investigated. We found that these were incorporated into another molecule of the starting material **1**. Thus, the reaction of **2a** with **1b** gave an equimolar amount of cyclohexanone with **9** (eq 5).

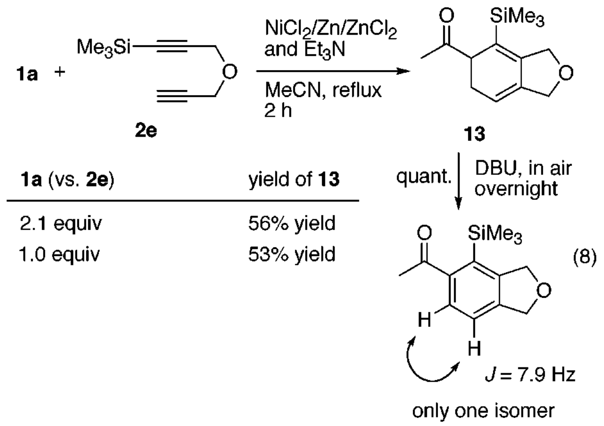


The reaction with **1c** (1.1 equiv vs **2a**), which could not be led to an aromatic cycloadduct, proceeded smoothly to give **10** in 65% yield (eq 6).



This binary metal system could be applied to the reaction of terminally mono- or disubstituted diynes. Ethyl-substituted diyne **2d** reacted with **1a** to give a mixture of 1,3-dienes **11a** and **11b** along with the corresponding aromatized compounds **12a** and **12b** (eq 7). However, the reaction of trimethylsilyl-substituted diyne **2e** smoothly proceeded with an equimolar amount of **1a** to afford 1,3-cyclohexadiene **13** regioselectively (eq 8). Neither the regioisomer nor their aromatized products were formed in the reaction. The structure of **13** was determined by the ^{1}H NMR spectra of the corresponding aromatized compound derived from treatment with DBU in air.[7]





1a (vs. **2e**)	yield of **13**
2.1 equiv	56% yield
1.0 equiv	53% yield

The results of the regioselective cycloaddition of **1a** with trimethylsilyl-substituted diynes are shown in Table 2. Diynes **2f** and **2g** also gave **14** and **15**, respectively. Diyne **2h** reacted with **1a** to give **16**, in which the trimethylsilyl group is adjacent to the acetyl group. Cyclohexadiene **17** containing a fused cyclohexane ring

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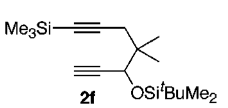
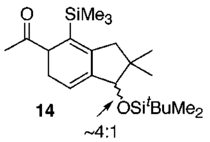
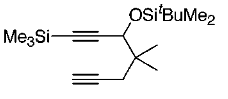
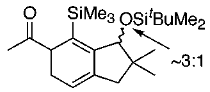
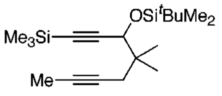
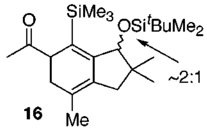
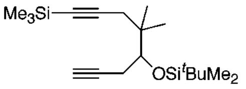
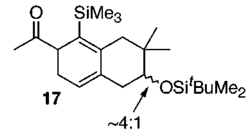
(8) The formation of **4** was identified by the GC/MS spectra (m/z = 472 (M^+)).

(9) Unidentified polymeric compounds would also be formed, causing incomplete material balances.

(10) For a nickel-catalyzed [2 + 2 + 2] cyclization of diynes and acetylene, see: Sato, Y.; Nishimata, T.; Mori, M. *J. Org. Chem.* **1994**, *59*, 6133 and references therein.

(11) Carbonaro, A.; Greco, A.; Dall'Asta, G. *Tetrahedron Lett.* **1968**, 5129. Singleton, D. M. *Tetrahedron Lett.* **1973**, 1245. Macomber, D. W.; Verma, A. G. *Organometallics* **1988**, *7*, 1241.

Table 2. Cycloaddition of 1a with Trimethylsilyl-Substituted Diynes[a]

diyne	product[b]	isolated yield, %
 **2f**	 **14** ~4:1	80
 **2g**	 **15** ~3:1	68
 **2h**	 **16**	63
 **2i**	 **17** ~4:1	64

[a] Reaction conditions: $NiCl_2$ (0.1 mmol), Zn dust (1.0 mmol), $ZnCl_2$ (1.4 mmol), Et_3N (1.5 mmol), **1a** (1.0 mmol), and diyne (1.0 mmol) in MeCn (4 mL) at reflux for 2 h. [b] Diastereoselectivity was determined by integration of the methyne protons in ^1H NMR.

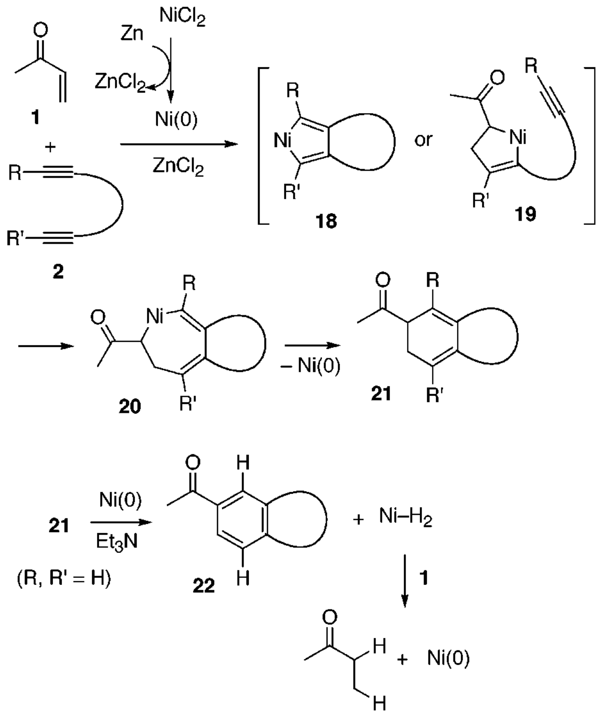
was formed from **2i**. The obtained regiochemically defined cycloadducts are attractive compounds because the trimethylsilyl group attached to an sp^2-carbon atom can be easily converted into various functional groups.[12]

A plausible mechanism for the present reaction is shown in Scheme 1. Metallacycle **18**[13] or **19**,[14] followed by intermediate **20**, is generated from Ni(0) species, **1**, and **2**. Reductive elimination of **20** gives 1,3-diene **21**. The regiochemically defined trimethylsilyl-substituted **21** (R = Me_3Si) is derived from the preferential coupling between the unsubstituted or methyl-substituted carbon–carbon triple bond in **2** (R′ = H or Me) and the carbon atom β-position in **1**, since the Me_3Si group acts as a deactivating substituent.[15] When both the R and R′ groups in **2a**–**c** are hydrogen atoms (R, R′ = H), the obtained 1,3-diene **21** would be easily dehydrogenated to give aromatized product **22** in the presence of Ni(0) species and Et_3N. The resulting nickel hydride (Ni–H_2) reacts with another molecule of **1** to regenerate Ni(0) species and also produces a saturated ketone.[16]

Conclusion

The nickel- and zinc-mediated [2 + 2 + 2] cycloaddition of diynes and enones had two interesting features. First, a terminally unsubstituted diyne reacted with enones (2 equiv vs diyne) to give an aromatized compound, rather than a 1,3-cyclohexadiene, with the concomitant incorporation of two hydrogen atoms into another molecule of the starting enone. On the other hand, the reaction of a trimethylsilyl-substituted diyne with an equimolar amount of enone regiospecifically gave a cyclohexadiene in which the trimethylsilyl group is adjacent to the carbonyl group. To the best of our knowledge, this is the first example of the completely regiochemically controlled cycloaddition of diynes and alkenes.

Scheme 1



Experimental Section

General. All reactions were carried out under a dry N_2 atmosphere. ^1H and ^{13}C NMR Spectra were recorded in $CDCl_3$ using Me_4Si as internal standard. Acetonitrile (MeCN) was distilled from P_2O_5. Zn dust was commercially available from Nacalai Tesque, Inc. and was used without activation procedure.

Typical Procedure. In a 20-mL three-necked flask were placed $NiCl_2$ (13 mg, 0.1 mmol), $ZnCl_2$ (190 mg, 1.4 mmol), Zn dust (66 mg, 1.0 mmol), MeCN (4 mL), and Et_3N (152 mg, 1.5 mmol), and the solution was stirred at room temperature for 5 min. To this suspension were added **2a** (236 mg, 1.0 mmol) and **1a** (148 mg, 2.1 mmol) at room temperature, and the mixture was then stirred at reflux for 2 h. After addition of aqueous HCl, the aqueous layer was extracted with Et_2O. The combined organic layers were washed successively with aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated in vacuo. Purification by silica gel column chromatography (hexane:AcOEt = 4:1) gave 235 mg (77%) of **3**.

Diethyl 5-acetylindan-2,2-dicarboxylate (3): a colorless oil; bp 165 °C (1.2 mmHg); R_f = 0.23 (hexane:AcOEt = 4:1); ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, J = 7.1 Hz, 6 H), 2.56 (s, 3 H), 3.61 (s, 4 H), 4.20 (q, J = 7.1 Hz, 4 H), 7.26 (d, J = 8.4 Hz, 1 H), 7.76–7.78 (m, 2 H); IR (neat) 1734, 1684 cm^{-1}; GC/MS (EI, 70 eV) m/z (rel int) 304 (M^+, 82), 230 (100). Anal. Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 66.84; H, 6.98.

5-Acetylisobenzofuran (7): a colorless oil; bp 150 °C (25 mmHg); R_f = 0.21 (hexane:AcOEt = 3:1); ^1H NMR (270 MHz, $CDCl_3$) δ 2.61 (s, 3 H), 5.14 (s, 4 H), 7.31 (d, J = 7.6 Hz, 1 H), 7.83–7.90 (m, 2 H); IR (neat) 1682 cm^{-1}; GC/MS (EI, 70 eV) m/z (rel int) 162 (M^+, 100). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 73.79; H, 6.27.

6-Acetyltetralin (8): a colorless oil; bp 130 °C (8 mmHg); R_f = 0.57 (hexane:AcOEt = 3:1); ^1H NMR (270 MHz, $CDCl_3$) δ

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[12] Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth: London, 1981; Chapter 7.

[13] For the nickelacyclopentadienes: Eisch, J. J.; Damasevitz, G. A. *J. Organomet. Chem.* **1975**, *96*, C19. Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1975**, *96*, C23. Hoberg, H.; Richter, W. *J. Organomet. Chem.* **1980**, *195*, 355. Eisch, J. J.; Aradi, A. A.; Han, K. I. *Tetrahedron Lett.* **1983**, *24*, 2073.

[14] (a) See ref 7. (b) Ikeda, S.; Kondo, K.; Sato, Y. *J. Org. Chem.* **1996**, *61*, 8248. (c) Montgomery, J.; Oblinger, E.; Savchenko, A. V. *J. Am. Chem. Soc.* **1997**, *119*, 4911.

[15] Tsuda, T.; Morikawa, S.; Hasegawa, N.; Saegusa, T. *J. Org. Chem.* **1990**, *55*, 2978.

[16] The added $ZnCl_2$ would act as a Lewis acid and activate **1**,[7] although the detail is unclear.

1.78−1.83 (m, 4 H), 2.55 (s, 3 H), 2.30−2.80 (m, 4 H), 7.13 (d, $J = 8.6$ Hz, 1 H), 7.64−7.67 (m, 2 H); IR (neat) 1682 cm^{-1}; GC/MS (EI, 70 eV) *m/z* (rel int) 174 (M$^+$, 30), 159 (100). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.47; H, 8.25.

7,7-Diethoxycarbonylcyclopenta[*g*]tetralone (9): a colorless oil; bp 190 °C (1.2 mmHg); $R_f = 0.21$ (hexane:AcOEt = 3:1); ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.23 (t, $J = 7.3$ Hz, 6 H), 2.02−2.12 (m, 2 H), 2.59 (t, $J = 6.4$ Hz, 2 H), 2.90 (t, $J = 6.0$ Hz, 2 H), 3.55 (s, 4 H), 4.18 (q, $J = 7.3$ Hz, 4 H), 7.07 (s, 1 H), 7.84 (s, 1 H); IR (neat) 1734, 1682 cm^{-1}; GC/MS (EI, 70 eV) *m/z* (rel int) 330 (M$^+$, 29), 256 (100). Anal. Calcd for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71. Found: C, 68.79; H, 6.75.

Diethyl 6*H*-5-formyl-5-methylindan-2,2-dicarboxylate (10): a colorless oil; bp 150 °C (7 mmHg); $R_f = 0.31$ (hexane: AcOEt = 3:1); ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.09 (s, 3 H), 1.20−1.26 (m, 6 H), 2.14 (ddd, $J = 17.8$, 6.7, 3.2 Hz, 1 H), 2.59 (ddt, $J = 17.8$, 4.6, 2.3 Hz, 1 H), 2.90−2.93 (m, 2 H), 2.95−2.99 (m, 2 H), 4.10−4.22 (m, 4 H), 5.29 (br s, 1 H), 5.50−5.57 (br s, 1 H), 9.42 (s, 1 H); IR (neat) 1732 cm^{-1}; GC/MS (EI, 70 eV) *m/z* (rel int) 306 (M$^+$, 0), 276 (28), 202 (100). Anal. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.43; H, 7.24.

Mixture of 11 and 12: a pale yellow oil; bp 150 °C (5 mmHg); $R_f = 0.34$ (hexane:AcOEt = 3:1); ^{1}H NMR of **11a** and **11b** (270 MHz, CDCl$_3$) δ 1.01 (t, $J = 7.6$ Hz, 3 H), 1.92−2.18 (m, 2 H), 2.16 (s, 3 H), 2.57−2.63 (m, 2 H), 3.09 (t, $J = 6.4$ Hz, 1 H), 4.35−4.42 (m, 2 H), 4.45−4.49 (m, 2 H), 5.35−5.41 (m, 1 H); GC/MS of **11** (EI, 70 eV) *m/z* (rel int) 192 (M$^+$, 4), 119 (100); HRMS of **11** for $C_{12}H_{14}O_2$ (M$^+$) calcd 190.0999, found 190.0993.

Mixture of 5-Acetly-4-ethylisobenzofuran (12a) and 4-Acetyl-6-ethylisobenzofuran (12b). These compounds were derived from the treatment of **11** with DBU in air; **12a**/**12b** = 6/1; a colorless crystal; bp 140 °C (4 mmHg); mp 34−36 °C (hexane); $R_f = 0.34$ (hexane:AcOEt = 3:1); ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.18 (t, $J = 7.6$ Hz, 3 H), 2.59 (s, 3 H), 2.75 (q, $J = 7.6$ Hz, 2 H), 5.15 (s, 4 H), 7.13 (d, $J = 7.7$ Hz, 0.86 H), 7.61 (d, $J = 7.7$ Hz, 0.86 H), 7.66 (br s, 0.14 H), 7.71 (br s, 0.14 H); IR (disk) 1684 cm^{-1}; GC/MS (EI, 70 eV) *m/z* (rel int) 190 (M$^+$, 70), 175 (100). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.53; H, 7.54.

5,6-Dihydro-5-acetyl-4-(trimethylsilyl)isobenzofuran (13): a colorless oil; bp 130 °C (4 mmHg); $R_f = 0.38$ (hexane: AcOEt = 3:1); ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.12 (s, 9 H), 2.14 (s, 3 H), 2.51−2.60 (m, 2 H), 3.18 (d, $J = 7.9$ Hz, 1 H), 4.36−4.40 (m, 2 H), 4.52 (s, 2 H), 5.55−5.58 (m, 1 H); IR (neat) 1703 cm^{-1}; DIMS (EI, 70 eV) *m/z* (rel int) 236 (M$^+$, 12), 73 (100). Anal. Calcd for $C_{13}H_{20}O_2Si$: C, 66.05; H, 8.53. Found: C, 66.18; H, 8.74.

5-Acetly-4-(trimethylsilyl)isobenzofuran: This compound (one isomer) was derived from the treatment of **13** with DBU in air; a colorless oil; bp 130 °C (3.5 mmHg); $R_f = 0.31$ (hexane:AcOEt = 4:1); ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.29 (s, 9 H), 2.62 (s, 3 H), 5.08 (s, 2 H), 5.17 (s, 2 H), 7.28 (d, $J = 7.9$ Hz, 1 H), 7.63 (d, $J = 7.9$ Hz, 1 H); IR (neat) 1686 cm^{-1}; GC/MS (EI, 70 eV) *m/z* (rel int) 234 (M$^+$, 0), 219 (M$^+$ − Me, 100). Anal. Calcd for $C_{13}H_{18}O_2Si$: C, 66.62; H, 7.74. Found: C, 66.87; H, 7.77.

5,6-Dihydro-5-acetyl-1-[(*tert*-butyldimethylsilyl)oxy]-2,2-dimethyl-4-(trimethylsilyl)indan (14): diastereoselectivity 80%; a colorless crystal; bp 120 °C (1.2 mmHg); $R_f = 0.40$ (hexane:AcOEt = 10:1); ^{1}H NMR of major isomer (80%) (270 MHz, CDCl$_3$) δ 0.05 (s, 3 H), 0.07 (s, 3 H), 0.12 (s, 9 H), 0.74 (s, 3 H), 0.92 (s, 9 H), 1.05 (s, 3 H), 2.10 (s, 3 H), 2.19 (d, $J = 16.0$ Hz, 1 H), 2.32 (d, $J = 16.0$ Hz, 1 H), 2.55−2.57 (m, 2 H), 3.05−3.08 (m, 1 H), 4.11−4.13 (m, 1 H), 5.53−5.55 (m, 1 H); the protons of minor isomer (20%) were also detected, δ 0.14 (s, 9 H), 0.87 (s, 9 H), 2.13 (s, 3 H), 3.86−3.89 (m, 1 H), 5.63−5.67 (m, 1 H); IR (disk) 1705 cm^{-1}; GC/MS (EI, 70 eV) *m/z* (rel int) 392 (M$^+$, 2), 73 (100). Anal. Calcd for $C_{22}H_{40}O_2Si_2$: C, 67.28; H, 10.27. Found: C, 67.01; H, 10.30.

5-Acetyl-1-[(*tert*-butyldimethylsilyl)oxy]-2,2-dimethyl-4-(trimethylsilyl)indan. This compound (one isomer) was derived from the treatment of **14** with DBU in air; a colorless crystal; mp 54.5−55.5 °C (hexane); bp 150 °C (1.2 mmHg); $R_f = 0.28$ (hexane:AcOEt = 10:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.16 (s, 3 H), 0.19 (s, 3 H), 0.28 (s, 9 H), 0.83 (s, 3 H), 0.97 (s, 9 H), 1.19 (s, 3 H), 2.59 (s, 3 H), 2.72 (d, $J = 15.3$ Hz, 1 H), 2.81 (d, $J = 15.3$ Hz, 1 H), 4.69 (s, 1 H), 7.25 (d, $J = 7.6$ Hz, 1 H), 7.48 (d, $J = 7.6$ Hz, 1 H); IR (disk) 1688 cm^{-1}; GC/MS (EI, 70 eV) *m/z* (rel int) 390 (M$^+$, 0), 375 (79), 333 (100). Anal. Calcd for $C_{22}H_{38}O_2Si_2$: C, 67.63; H, 9.80. Found: C, 67.56; H, 9.88.

5,6-Dihydro-6-acetyl-1-[(*tert*-butyldimethylsilyl)oxy]-2,2-dimethyl-7-(trimethylsilyl)indan (15): diastereoselectivity 75%; a colorless oil; bp 105 °C (1.3 mmHg); $R_f = 0.49$ (hexane:AcOEt = 10:1); ^{1}H NMR of major isomer (75%) (270 MHz, CDCl3) δ 0.09 (s, 3 H), 0.13 (s, 3 H), 0.19 (s, 9 H), 0.71 (s, 3 H), 0.86 (s, 9 H), 1.07 (s, 3 H), 2.18 (s, 3 H), 2.34−2.51 (m, 4 H), 3.22 (dd, $J = 8.2$, 5.2 Hz, 1 H). 4.16 (s, 1 H), 5.48−5.60 (m, 1 H); the protons of minor isomer (25%) were also detected, δ −0.002 (s, 3 H), 0.04 (s, 3 H), 0.15 (s, 9 H), 0.85 (s, 9 H), 0.88 (s, 3 H), 1.10 (s, 3 H), 2.17 (s, 3 H), 3.13 (dd, $J = 7.9$, 3.1 Hz, 1 H), 4.18 (s, 1 H); IR (disk) 1707 cm^{-1}; GC/MS of major isomer (EI, 70 eV) *m/z* (rel int) 392 (M$^+$, 1), 335 (100); GC/MS of minor isomer (EI, 70 eV) *m/z* (rel int) 392 (M$^+$, 20), 73 (100). Anal. Calcd for $C_{22}H_{40}O_2Si_2$: C, 67.28; H, 10.27. Found: C, 67.14; H, 10.29.

6-Acetyl-1-[(*tert*-butyldimethylsilyl)oxy]-2,2-dimethyl-7-(trimethylsilyl)indan. This compound (one isomer) was derived from the treatment of **15** with DBU in air; a colorless oil; bp 105 °C (1.5 mmHg); $R_f = 0.49$ (hexane:AcOEt = 10:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ −0.42 (s, 3 H), −0.24 (s, 3 H), 0.36 (s, 9 H), 0.83 (s, 3 H), 0.82 (s, 9 H), 0.87 (s, 3 H), 1.24 (s, 3 H), 2.40 (d, $J = 16.5$ Hz, 1 H), 2.59 (s, 3 H), 3.03 (d, $J = 16.5$ Hz, 1 H), 4.94 (s, 1 H), 7.25 (d, $J = 7.6$ Hz, 1 H), 7.61 (d, $J = 7.6$ Hz, 1 H); IR (disk) 1688 cm^{-1}; GC/MS (EI, 70 eV) *m/z* (rel int) 390 (M$^+$, 0), 333 (M$^+$ − ^{t}Bu, 67), 243 (100). Anal. Calcd for $C_{22}H_{38}O_2Si_2$: C, 67.63; H, 9.80. Found: C, 67.34; H, 9.75.

5,6-Dihydro-6-acetyl-1-[(*tert*-butyldimethylsilyl)oxy]-2,2-dimethyl-4-methyl-7-(trimethylsilyl)indan (16): diastereoselectivity 67%; a colorless oil; bp 124 °C (1.0 mmHg); $R_f = 0.40$ (hexane:AcOEt = 10:1); ^{1}H NMR of major isomer (67%) (400 MHz, CDCl$_3$) δ 0.07 (s, 3 H), 0.12 (s, 3 H), 0.17 (s, 9 H), 0.69 (s, 3 H), 0.86 (s, 9 H), 1.08 (s, 3 H), 1.70 (s, 3 H), 2.16 (s, 3 H), 2.21?2.56 (m, 4 H), 3.25 (t, $J = 7.1$ Hz, 1 H), 4.16 (s, 1 H); ^{1}H NMR of minor isomer (33%) (400 MHz, CDCl$_3$) δ ?0.057 (s, 3 H), 0.01 (s, 3 H), 0.15 (s, 9 H), 0.85 (s, 3 H), 0.84 (s, 9 H), 1.11 (s, 3 H), 1.69 (s, 3 H), 2.09 (s, 3 H), 2.21−2.56 (m, 4 H), 3.12 (br s, 1 H), 4.18 (s, 1 H); IR (neat) 1707 cm^{-1}; GC/MS of major product (EI, 70 ev) *m/z* (rel int) 406 (M$^+$, 1), 73 (100); GC/MS of minor product (EI, 70 ev) *m/z* (rel int) 406 (M$^+$, 4), 73 (100); HRMS for $C_{23}H_{42}O_2Si_2$ (M$^+$, major isomer) calcd 406.2723, found 406.2724; HRMS for $C_{23}H_{42}O_2Si_2$ (M$^+$, minor isomer) calcd 406.2723, found 406.2731.

6,7-Dihydro-6-acetyl-2-[(*tert*-butyldimethysilyl)oxy]-3,3-dimethyl-5-(trimethylsilyl)tetralin (17): diastereoselectivity 82%; a colorless crystal; mp 80−81 °C (hexane); $R_f = 0.60$ (hexane:AcOEt = 11:1); ^{1}H NMR of major isomer (82%) (400 MHz, CDCl$_3$) δ 0.038 (s, 6 H), 0.20 (s, 9 H), 0.83 (s, 3 H), 0.88 (s, 9 H), 0.97 (s, 3 H), 2.00 (d, $J = 15.3$ Hz, 1 H), 2.07 (s, 3 H), 2.11?2.25 (m, 2 H), 2.36 (dd, $J = 16.2$, 6.0 Hz, 1 H), 2.46 (d, $J = 15.3$ Hz, 1 H), 2.58 (dd, $J = 16.2$, 6.0 Hz, 1 H), 2.83−2.85 (m, 1 H), 3.44−3.48 (m, 1 H), 5.55−5.60 (m, 1 H); the protons of minor isomer (18%) were also detected, δ 0.86 (s, 9 H), 5.51−5.52 (m, 1 H); IR (neat) 1709 cm^{-1}; GC/MS (EI, 70 eV) *m/z* (rel int) 406 (M$^+$, 3), 73 (100); HRMS for $C_{17}H_{27}OSi$ (M$^+$ − OSi^{t}BuMe$_2$) calcd 275.1831, found 275.1831.

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Supporting Information Available: Spectral data for **2e**−**i**, ^{13}C NMR spectral data for **3**, **7**−**10**, **12a**, and **13**−**17**, and ^{13}C NMR spectra for **14**−**17** and the aromatized compounds of **14** and **15** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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