crystallizations from benzene-hexane afforded white crystals, mp 236–237 °C.

Anal. Calcd for $C_{30}H_{30}$: C, 92.31; H, 7.69. Found: C, 92.21; H, 7.74.

The IR and NMR spectra were essentially identical to those of the product formed by dehydrotrimerization.

A second fraction, 15 mg, mp 79–82 °C, of slightly higher R_f value, exhibited a molecular ion (*m/e* 272) in the mass spectrum corresponding to the molecular weight of 2 (lit.[21] mp 88–91 °C).

Acknowledgment. We are grateful to the National Science Foundation, Polymers Program, Division of Materials Research, Grant No. DMR75-06788, for support of this work, to Mr. Paul Karges for mass spectral data, and to Dr. Kathryn N. McFarland for assistance.

Registry No.—1, 65879-27-8; $CuCl_2$, 7447-39-4; $AlCl_3$, 7446-70-0; TCNE, 670-54-2; chloranil, 118-75-2; chlorobenzene, 108-90-7; benzidine, 92-87-5; *N,N'*-dinitroso-*N,N'*-diacetylbenzidine, 61444-52-8.

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Rhodium Catalysis of Allylic Oxidations with Molecular Oxygen. β-Silyl-2-cycloalkenones

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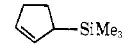
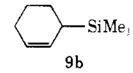
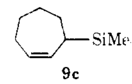
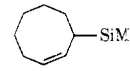
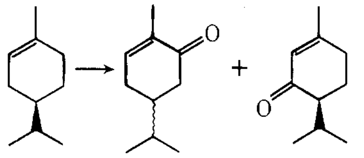
Rhodium catalyzed autoxidation of cycloalkenes with allylic carboethoxyl, isopropyl, and trimethylsilyl substituents is examined. Reaction of 3-(trimethylsilyl)cycloalkenes with molecular oxygen in the presence of tris(triphenylphosphine)rhodium(I) chloride is regiospecifc and affords β-silylcycloalken-2-ones in good yields. A new rhodium-catalyzed allylic oxidation reaction is reported which utilizes *tert*-butyl hydroperoxide as oxidizing agent.

Ten years ago, chlorotris(triphenylphosphine)rhodium(I) (1) was shown to catalyze allylic oxidation of olefins[1,2] by molecular oxygen. Cyclohexen-3-one and water are major products of the catalyzed autoxidation of cyclohexene. Since 1 forms coordination complexes with oxygen, it was considered that the catalyst might function by activating molecular oxygen. That is, coordination of oxygen would be prerequisite for catalysis. However, $Rh(CO)(PPh_3)_2Cl$, which interacts only weakly with oxygen, shows similar catalytic activity and product distribution as 1.[3] Furthermore, autoxidations of cyclohexene catalyzed by cobalt(II) carboxylates yield almost identical product mixtures as reactions catalyzed by 1, and the latter reactions are completely inhibited by 2% of hydroquinone[4a] as is rhodium(I) promoted autoxidation of tetramethylethylene.[4b] These observations suggest that autoxidations catalyzed by 1, in analogy with cobalt, are free radical chain reactions in which the metal complex initiates chains by inducing decomposition of hydroperoxides. How-

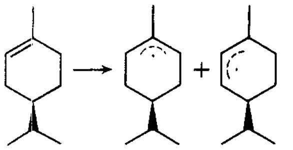
Table I. Synthesis of 3-(Trimethylsilyl)cycloalkenes

Silane	Registry no.	Bp (yield, %)	^{1}H NMR (in CCl_4)
 9a	14579-08-9	140–146 °C (94)	0.00 (s, 9 H, $SiCH_3$), 1.68–258 (m, 5 H, CH_2's, CH), 5.66 (s, 2 H, CH=CH)
 9b	40934-71-2	69–72 °C (10 mm) (54)	0.00 (s, 9 H, $SiCH_3$), 1.3–2.2 (broad m, 7 H, CH_2's, CH), 5.60 (s, 2 H, CH=CH)
 9c	66085-02-7	85–95 °C (8 mm) (32)	0.00 (s, 9 H, $SiCH_3$), 1.3–2.4 (broad m, 9 H, CH_2's, CH), 5.53–5.75 (m, 2 H, CH=CH)
 9d	20083-09-4	60–70 °C (0.45 mm) (22)	0.00 (s, 9 H, $SiCH_3$), 1.1–2.5 (broad m, 11 H, CH_2's, CH), 5.2–5.9 (m, 2 H, CH=CH)

ever, for metal-catalyzed autoxidation, inhibitors could operate by reaction with the catalyst rather than by scavenging radicals.[4d] Further evidence considered to support allyl radical intermediates was obtained from the autoxidation of (+)-carvomenthene (2) promoted by 1.[5] This reaction gives carvotanacetone (3) and piperitone (4), and several derived alcohols. Though 2 is not racemized under the reaction conditions, 3 is completely racemic. A symmetrical intermediate, such as the radical 5, is thus implicated in the pathway from 2 to 3. An analogous intermediate 6 leads to 4. However, η^3-allylrhodium intermediates (i.e., rhodium complexes of 5 and 6), which also could explain formation of racemic 3, have not been ruled out.

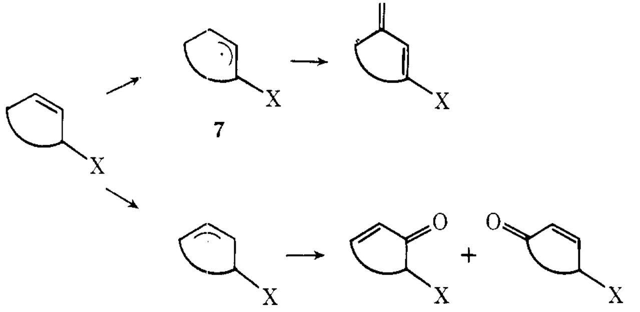


2 3 4



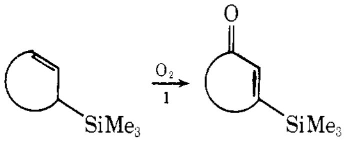
2 5 6

Molecular oxygen is an inexpensive oxidant for organic synthesis. Homogeneous catalysis enhances the utility of this reagent by permitting controlled oxidations under mild conditions. However, such oxidations (e.g., 2 → 3 + 4) generally give complex product mixtures which are difficult to separate since hydrogen atom abstraction and subsequent capture of intermediate allyl radicals are nonregiospecific. It seems reasonable that an allylic substituent which facilitates hydrogen abstraction should promote oxidation and favor products from allyl radicals of type 7 over those from 8. We now report that 1 catalyzes regiospecific oxidation of cyclic allylsilanes (9) to afford β-silyl-2-cycloalkenones (10) in good yields.



7

8

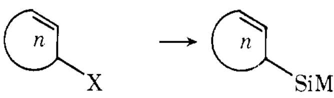


9 10

Results and Discussion

Rhodium catalyzed oxidations of cycloalkenes with allylic substituents including carboethoxyl, isopropyl, and trimethylsilyl groups were examined. Only the trimethylsilyl derivatives underwent synthetically valuable oxidations in goods yields. Oxygen is an oxidizing reagent of choice, but we also discovered that *tert*-butyl hydroperoxide can serve as the oxidizing reagent with chlorotris(triphenylphosphine)rhodium(I) (1) as a catalyst.

Synthesis of 3-(Trimethylsilyl)cycloalkenes. Hydrosilation of 1,3-cyclopentadiene with trichlorosilane and methylation of the resulting 3-(trichlorosilyl)cyclopentene with methylmagnesium bromide afford 3-(trimethylsilyl)cyclopentene (9a) in moderate yield.[6] Alternatively, 1,3-cyclopentadiene is readily converted into 3-chlorocyclopentene (11a),[7] and 9a is prepared by addition of an equimolar mixture of 11a and chlorotrimethysilane in tetrahydrofuran (THF) to magnesium turnings.[8] We obtained 9a in excellent yield (see Experimental Section) by a modification of the latter procedure. Thus, 11a in THF is added to a mixture of magnesium turnings and a solution of excess chlorotrimethylsilane in THF. This procedure, which is the method of choice, is noteworthy since allylic silanes are useful synthons for organic synthesis.[4b,9] This method is analogous to that reported for the synthesis of 9b from 11b.[10] The method is less satisfactory for the seven- and eight-membered analogues 9c and 9d (see Table I).

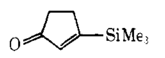
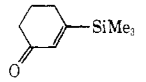
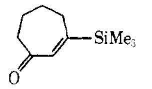
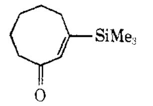


11a, $n = 5$; X = Cl
b, $n = 6$; X = Br
c, $n = 7$; X = Br
d, $n = 8$; X = Br

9a, $n = 5$
b, $n = 6$
c, $n = 7$
d, $n = 8$

Rhodium(I) Catalyzed Autoxidation of 3-Substituted Cycloalkenes. A slow stream of oxygen was bubbled through solutions of tris(triphenylphosphine)rhodium(I) chloride (1 mol %) in pure olefin at 100 °C. Reaction progress was monitored by gas–liquid phase chromatography (GLPC). Complete

Table II. Rhodium Catalyzed Autoxidation of 3-(Trimethylsilyl)cycloalkenes

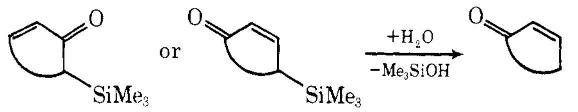
Oxidation[a] product **10**	Registry no.	Bp (yield, %)[b]	^{1}H NMR (in CCl$_4$)
 **a**	66085-03-8	90 °C (9.5 mm) (83)	0.20 (s, 9 H, SiCH$_3$), 1.95–2.34 (m, 2 H, CH$_2$), 2.50–2.83 (m, 2 H, CH$_2$), 6.25 (t, 1 H, J = 2.0 Hz, CH)
 **b**	66085-04-9	84 °C (4.0 mm) (81)	0.13 (s, 9 H, SiCH$_3$), 1.70–2.50 (m, 6 H, CH$_2$'s), 5.90 (m, 1 H, CH)
 **c**	66085-05-0	72 °C (0.68 mm) (84)	0.13 (s, 9 H, SiCH$_3$), 1.62–1.90 (m, 4 H, 2 CH$_2$), 2.33–2.62 (m, 4 H, 2 CH$_2$), 6.15 (m, 1 H, CH)
 **d**	66085-06-1	38% SM recovered[c] (60)	0.14 (s, 9 H, SiCH$_3$), 1.40–2.10 (broad s, 6 H, 3 CH$_2$), 2.45–2.80 (broad s, 4 H, 2 CH$_2$), 6.24 (s, 1 H, CH)

[a] Oxidation reactions run at 97 °C. Times required for completion: entry (time, h) **10a** (1.5), **10b** (1.5), **10c** (4.5), **10d** (2); were determined by GLPC monitoring of the reactions with a $\frac{1}{8}$ in. × 10 ft column filled with 10% SE-30 on 60/80 Chromosorb W at 200 °C. [b] Yields are for pure products isolated by distillation except for **10d** (see Experimental Section). [c] By the *tert*-butyl hydroperoxide method (see text).

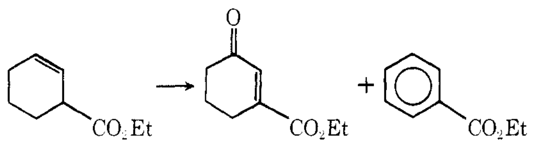
oxidation of the allylic silanes **9a–9c** required 1.5–4.5 h. The β-silylcycloalkenone products **10a–10c** were separated from catalyst by transfer under reduced pressure (0.2 mm) into a cold trap (−78 °C), and isolated in good yields by distillation under reduced pressure (see Table II). The recovered catalyst showed unattenuated activity for promoting autoxidation of a second batch of 3-(trimethylsilyl)cycloalkene.

Autoxidation of 3-(trimethylsilyl)cyclooctene (**9d**) promoted by rhodium catalyst **1** was sluggish. We discovered that inclusion of *tert*-butyl hydroperoxide (*t*-BHP) in the autoxidation reaction mixtures noticeably increased the rate of oxidation. Thus, with two equivalents of *t*-BHP **9d** underwent 62% conversion upon heating with oxygen for 2 h. The yield of ketone **10d** was 60% according to GLPC analysis of the reaction mixture.

Although only isomerically pure β-silyl-α,β-unsaturated ketones were isolated, we considered the possibility that minor amounts of isomeric α'- or γ-silyl-α,β-unsaturated ketones may be formed. These products are expected to be selectively destroyed by facile protodesilation under the reaction conditions.[11] However, meticulous examination of the oxidation product mixture from 3-(trimethylsilyl)cyclopentene (**9a**) revealed no trace of 2-cyclopenten-1-one.

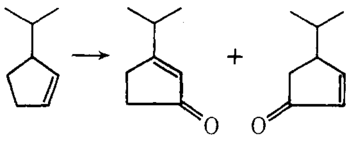


Autoxidation of ethyl cyclohex-2-enecarboxylate (**12**) also was facilitated by *t*-BHP in addition to the rhodium complex (**1**). Thus, **12** underwent 51% conversion upon heating with oxygen for 5 h in the presence of **1** and 2 equiv of *t*-BHP. The only ketone product was ethyl 3-oxo-1-cyclohexene-1-carboxylate (**13**) in 77% yield. Also, ethyl benzoate was produced in 23% yield. Attempted complete conversion of **12** resulted in decreased yields of **13** which apparently is slowly destroyed upon prolonged heating of the reaction mixture.



12 **13**

Autoxidation of 3-isopropylcyclopent-1-ene (**14**) in the presence of **1** resulted in 58% conversion after 4 h. Two isomeric oxidation products, 3-isopropylcyclopent-2-en-1-one (**15**) and 4-isopropylcyclopent-2-en-1-one (**16**), were produced in 42% and 11% yields, respectively. Again, attempted complete conversion of the alkene resulted in decreased yields of enone products. The lack of complete regiospecificity in the oxidation of **14** shows that the isopropyl group does not promote cleavage of an allylic carbon–hydrogen bond as effectively as a carboethoxyl or trimethylsilyl group. In fact, the ratio of **15** to **16** observed may be an overestimate of the actual regiospecificity of hydrogen atom abstraction from **14** since the complex **1** promotes isomerization of **16** into **15**.[12]

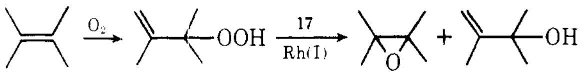


14 **15** **16**

Autoxidation of 3-(Trimethylsilyl)cyclopentene Initiated by Benzoyl Peroxide. If autoxidations catalyzed by **1** are free radical chain reactions in which the metal complex serves only to initiate chains (e.g., by inducing decomposition of hydroperoxides), then similar autoxidations should be possible with other radical initiators such as benzoyl peroxide. A slow stream of oxygen was bubbled through a solution of benzoyl peroxide (1 mol %) in pure 3-(trimethylsilyl)cyclopentene (**9a**) at 100 °C for 4 h. Transfer of the oxidation product into a cold trap as above gave 3-(trimethylsilyl)cyclopent-2-en-1-one (**10a**), isomerically pure, but in only 12% yield. In addition, 3-(trimethylsilyl)cyclopent-2-en-1-ol was obtained in 28% yield. The remaining products consisted of a nonvolatile viscous oil. No trace of 2-cyclopenten-1-one was detected. Thus, the same high regioselectivity is observed in autoxidations promoted by benzoyl peroxide and by the rhodium catalyst **1**. This suggests that the regioselectivity in both reactions is totally determined by the silyl substituent. That is, an olefin–rhodium interaction need not be invoked to explain the regioselectivity of the rhodium catalyzed oxidations.

Rhodium(I) Catalyzed Allylic Oxidation of 3-(Trimethylsilyl)cyclopentene with *tert*-Butyl Hydroperoxide. One function of rhodium in promoting autoxidation of olefins is believed to be catalysis of hydroperoxide decomposition to produce chain-initiating radicals.[3-5] Hydroperoxides are intermediate products which may arise via capture of allyl radicals with molecular oxygen. In some cases, allylic hydroperoxides can be isolated from rhodium promoted autoxidation of olefins.[4] Although rhodium(I) forms complexes with molecular oxygen, it has been argued that the catalytic action of rhodium(I) complexes in allylic oxidation of olefins does not involve activation of oxygen by coordination.[3-5] However, recent work suggests that this question deserves further scrutiny.[4d] Coordination of the olefin substrate by the metal catalyst is definitely not a prerequisite for catalysis.[4b]

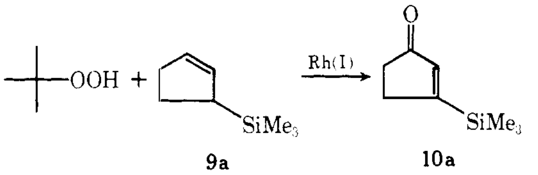
Besides generating chain-initiating radicals, the interaction of hydroperoxide intermediates with the rhodium catalyst can also result in oxidation of the olefin substrate. For example, a rhodium(I) catalyst promotes a reaction between a hydroperoxide intermediate (**18**) from autoxidation of tetramethylethylene (**17**) and the olefin **17** to afford epoxide and tertiary allylic alcohol **20**.[4b] Similarly, **17** or styrene reacts with *t*-BHP



17 **18** **19** **20**

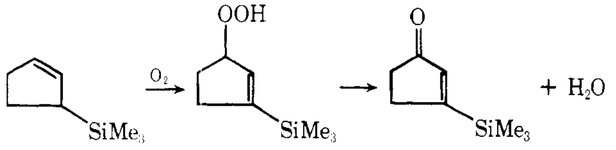
in the presence of a rhodium catalyst, but in the absence of oxygen, to afford **19** or styrene oxide, respectively, as well as *tert*-butyl alcohol.[13]

It was of interest to determine if hydroperoxides react with 3-substituted cycloalkenes (e.g., **9**) in the presence of rhodium catalyst **1** to afford allylic oxidation products (e.g., **10**). Thus, allylsilane **9a** was heated with 2 equiv of *t*-BHP and 1 mol % of the rhodium catalyst **1** *in the absence of molecular oxygen*. After 20 h at 74 °C, **9a** underwent 87% conversion to **10a** in 57% yield.

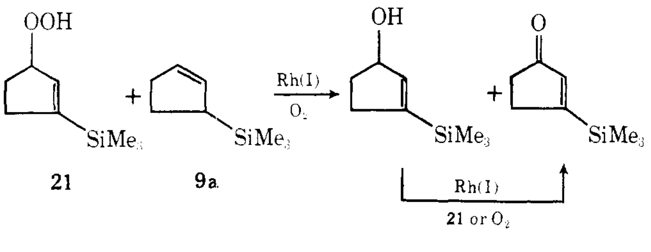


9a **10a**

The ketone **10a** could be produced exclusively by loss of water from an intermediate hydroperoxide **21** in the autoxidation of **9a** catalyzed by rhodium(I). However, the reaction described above between *t*-BHP and **9a** to give **10a** suggests that some of the **10a** produced in the reaction of **9a** with molecular oxygen may arise via a rhodium catalyzed reaction of **21** with **9a**. The dependence of reaction products and kinetics from cyclohexene on reaction conditions shows the mechanistic complexity of some rhodium promoted autoxidations.[1,4d] Our demonstration that hydroperoxides can serve as oxidizing agents in rhodium promoted allylic oxidations further complicates the mechanistic picture for rhodium catalysis of autoxidations.



9a **21** **10a**



21 **9a**

Whatever the mechanism, the ready availability of allylsilanes, mild reaction conditions, regiospecificity of the rhodium promoted autoxidations, and the good yields of pure β-silylcycloalken-2-ones obtained make this approach attractive for preparative purposes. Moreover, methods described previously for synthesis of β-silyl-α,β-unsaturated ketones are *not* applicable for preparation of *cyclic* silyl enones.[14] The versatility of vinylsilanes in organic synthesis increases the potential applications of this approach.[15] In addition, vinylsilanes are readily protodesilylated to afford the corresponding olefins. Thus, **10a** gives 2-cyclopentenone quantitatively by reaction with dry HCl in THF.

Experimental Section

General. All preparative GLPC work was performed with a Varian Model 90-P chromatograph using a 6 ft × ¼ in. column filled with 15% SE-30 silicone oil on 60/80 Chromosorb W. Analytical GLPC work was performed with a Varian series 1200 chromatograph using a 10 ft × ⅛ in. column filled with 10% SE-30 silicone oil on 60/80 Chromosorb W. ^{1}H NMR spectra were recorded with a Varian A60A or HA-100 with Fourier transform using CCl_4 as solvent and 1% Me_4Si as internal standard. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz.

Synthesis of Cyclic Allylsilanes. General Procedure. Chlorotrimethylsilane (64.7 mL, 0.51 mol), magnesium (18.7 g, 0.77 mmol), and THF (250 mL, freshly distilled from sodium benzophenone ketyl) were placed into a flame-dried three-necked flask fitted with reflux condenser, addition funnel, mechanical stirrer, and nitrogen inlet tube. The mixture was cooled to 5 °C in an ice bath. The addition funnel was charged with the allyl halide (0.51 mol) and dry THF (500 mL), and cooled with a dry ice jacket. The resulting solution was added dropwise over several hours. The reaction was allowed to warm to room temperature and was stirred overnight. The reaction product was washed with water (5 × 100 mL) and the aqueous layers were backwashed with pentane (50 mL). The combined organic fractions were washed with saturated NaCl (100 mL) and dried ($MgSO_4$). After filtering, the solvent was removed by rotary evaporation and the product was distilled. Physical constants are listed in Table I.

3-(Trimethylsilyl)cyclopentene (9a) and 3-(trimethylsilyl)cyclohexene (9b) were reported previously.[8,10]

3-(Trimethylsilyl)cycloheptene (9c). Anal. Calcd for $C_{10}H_{20}Si$: C, 71.34; H, 11.97. Found: C, 70.76; H, 11.56.

3-(Trimethylsilyl)cyclooctene (9d). Anal. Calcd for $C_{11}H_{22}Si$: C, 72.44; H, 12.16. Found: C, 72.44; H, 12.38.

Rhodium Catalyzed Autoxidations: β-Silyl-2-cycloalkenones. The procedure for oxidation of 3-(trimethylsilyl)cyclopent-1-ene is typical. 3-(Trimethylsilyl)cyclopent-1-ene (500 mg, 3.56 mmol) and **1** (33 mg, 1 mol %) were placed in a 5-mL round-bottom flask equipped with reflux condenser, stirring bar, and oxygen inlet tube such that the gas was slowly bubbled in under the liquid surface. The mixture was then heated for 1.5 h with stirring at 97 °C (oil bath). After cooling, the reaction mixture was vacuum transferred to remove the catalyst. For larger scale reactions the product was distilled under reduced pressure. Physical data are given in Table I.

3-(Trimethylsilyl)cyclopent-2-en-1-one (10a). Anal. Calcd for $C_8H_{14}SiO$: C, 62.27; H, 9.14. Found: C, 62.58; H, 9.12.

3-(Trimethylsilyl)cyclohex-2-en-1-one (10b). Anal. Calcd for $C_9H_{16}SiO$: C, 64.22; H, 9.58. Found: C, 64.24; H, 9.70.

3-(Trimethylsilyl)cyclohept-2-en-1-one (10c). Anal. Calcd for $C_{10}H_{18}SiO$: C, 65.85; H, 9.95. Found: C, 65.61; H, 10.02.

Oxidation of 3-Isopropylcyclopent-1-ene. 3-Isopropylcyclopent-1-ene (**14**) (500 mg, 4.54 mmol) and **1** (42 mg, 1 mol %) were placed in a 5-mL round-bottomed flask fitted with reflux condenser and oxygen inlet tube as described above. The mixture was heated with magnetic stirring in an oil bath at 97 °C for 4 h. After vacuum transfer the following major components were isolated by GLPC: entry, absolute % yield (relative GC retention time); starting material **14**, 42% (1.0); 4-isopropylcyclopent-2-en-1-one (**16**), 11% (2.0); 3-isopropylcyclopent-2-en-1-one (**15**), 42% (2.6). The enone **15** was characterized by the identity of its ^{1}H NMR spectrum with that reported.[16] The structural assignment for the isomeric enone **16** is based on its ^{1}H NMR spectrum: (CCl_4) δ 0.95 and 0.99 (6 H, 2 doublets, J = 6 Hz, 2 CH_3's, 1:1 mixture of diastereomers), 1.74 (1 H, m, CH), 1.92 (1 H, dd, J = 4, 18 Hz, CH_2), 2.30 (1 H, dd, J = 6, 18 Hz, CH_2), 2.70

(1 H, m, CH), 6.10 (1 H, dd, *J* = 2, 6 Hz, C-2 vinyl), 7.52 (1 H, dd, *J* = 2, 6 Hz, C-3 vinyl).

4-Isopropylcyclopent-2-en-1-one (**16**) was further characterized by isomerization to **15** in the presence of rhodium(I) complex (**1**). A small sample of 4-isopropylcyclopent-2-en-1-one (**16**) was isolated by GLPC and placed in a sealed NMR tube with **1** (5 mg) and CCl_4. The tube was heated at 80 °C. The ^1H NMR spectrum of the solution after 15 h showed only 3-isopropylcyclopent-2-en-1-one (**15**).

Oxidation of 3-(Trimethylsilyl)cyclopent-1-ene (9a) with Recovered Catalyst. The rhodium containing residue, from oxidation of **9a** with oxygen, and 3-(trimethylsilyl)cyclopent-1-ene (500 mg, 3.56 mmol) were placed in a flask fitted with reflux condenser and oxygen inlet tube as described above. The resulting mixture was heated in an oil bath at 98 °C. After 1 h the reaction was complete, yielding 467 mg (85%) of vacuum transferred product (90% pure by GLPC).

Rhodium Catalyzed Oxidation of 9a with *tert*-Butyl Hydroperoxide. 3-(Trimethylsilyl)cyclopent-1-ene (**9a**) (100 μL), undecane (20 μL, as internal standard), and *tert*-butyl hydroperoxide (200 μL) were vacuum sealed in a Pyrex tube and heated in an oil bath at 74 °C for 20 h. GLPC analysis of the crude reaction mixture showed 13% starting material and 50% of β-trimethylsilyl-2-cyclopentenone (**10a**).

***tert*-Butyl Hydroperoxide Assisted Autoxidation of 3-(Trimethylsilyl)cyclooct-1-ene.** 3-(Trimethylsilyl)cyclooct-1-ene (**9d**) (500 mg, 2.54 mmol), **1** (23 mg, 1 mol %), and *tert*-butyl hydroperoxide (510 μL, 5.08 mmol) were placed in a 10-mL round-bottomed flask equipped with reflux condenser, magnetic stirring bar, and oxygen inlet tube as previously described. The resulting mixture was heated in an oil bath at 96 °C for 2 h. The reaction product was then analyzed by GLPC (see Table I). A sample of **10d** was isolated for analysis by GLPC.

3-(Trimethylsilyl)cyclooct-2-en-1-one (10d). Anal. Calcd for $C_{11}H_{20}SiO$: C, 67.28; H, 10.27. Found: C, 67.52; H, 10.52.

***tert*-Butyl Hydroperoxide Assisted Oxidation of Ethyl Cyclohex-2-enecarboxylate (12).** Ethyl cyclohex-2-enecarboxylate (**12**)[17] (500 mg, 3.24 mmol), **1** (30 mg, 1 mol %), and *tert*-butyl hydroperoxide (0.70 mL, 6.48 mmol) were placed in a 5-mL round-bottom flask fitted with reflux condenser and O_2 delivery tube as described above and heated in an oil bath at 96 °C for 5 h. The following components were isolated by GLPC: entry, absolute yield % (relative GC retention time); starting material **12**, 34% (1.0); ethyl benzoate, 15% (1.1); ethyl 3-oxo-1-cyclohexene-1-carboxylate (**13**), 51% (2.1). The enone **13** was characterized by the identity of its ^1H NMR spectrum with that reported.[18]

Protonolysis of 3-(Trimethylsilyl)cyclopent-2-en-1-one (10a). A typical protonolysis procedure follows. 3-(Trimethylsilyl)cyclopent-2-en-1-one (500 mg, 3.24 mmol) in dry THF (15 mL) was saturated with dry HCl and boiled under reflux under nitrogen for 14 h. The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted into pentane (25 mL). The organic layer was dried ($MgSO_4$), and the solvent was removed by rotary evaporation. A quantitative yield of cyclopentenone was obtained.

Benzoyl Peroxide Initiated Autoxidation of 3-(Trimethylsilyl)cyclopentene. The olefin **9a** (2.5 g, 18 mmol) and benzoyl peroxide (43 mg) were placed in a 15-mL round-bottom flask equipped with reflux condenser, oxygen inlet tube which entered through the top of the condenser, and gas outlet near the top of the condenser. Oxygen was slowly bubbled in under the liquid surface while the reaction mixture was heated at 97 °C (oil bath) for 4 h. The volatile products were then transferred under reduced pressure (0.2 Torr) into a cold receiver (−78 °C). Yields were determined by ^1H NMR analysis of the product mixture, and **3-(trimethylsilyl)cyclopent-2-en-1-ol** was isolated by preparative gas–liquid phase chromatography. ^1H NMR: (CCl_4) δ 0.07 (9 H, s, $SiMe_3$), 1.33–2.58 (5 H), 4.57–4.88 (H, m, CH–O), 5.85–6.02 (H, m, vinyl). Anal. Calcd for $C_8H_{16}SiO$: C, 61.47; H, 10.32. Found: C, 61.56; H, 10.38.

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Registry No.—**1**, 14694-95-2; **11a**, 96-40-2; **11b**, 1521-51-3; **11c**, 36291-49-3; **11d**, 7422-06-2; **12**, 55510-68-4; **13**, 25017-79-2; **14**, 4276-45-3; **15**, 1619-28-9; **16**, 54814-23-2; chlorotrimethylsilane, 75-77-4; 3-(trimethylsilyl)cyclopent-2-en-1-ol, 66085-07-2.

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