Organometallics 1994, *13*, 1656–1661

Cyclocarbonylation of 1,6-Enynes Promoted by Iron Carbonyls

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Received December 29, 1993⊛

Iron carbonyls have been found to promote the cyclocarbonylation of 1,6-enynes to give cyclopentenones in good yield. The reaction is essentially the same as the intramolecular Pauson–Khand reaction. The best results were obtained using allyl propargyl ethers as substrates. Isomerization of the alkene moiety competes with cyclization in some cases, leading to reduced yields. Stereoselectivity comparable with that obtained in the Pauson–Khand reaction was observed during the cyclization of alkoxy-substituted enynes; this stereoselectivity appears to be kinetic rather than thermodynamic.

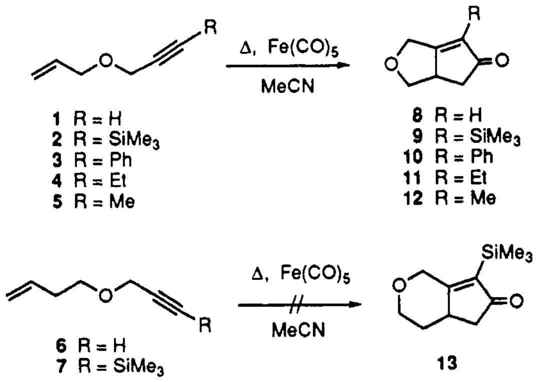
Introduction

The now well-known intramolecular Pauson–Khand reaction[1] has been extensively investigated and provides a powerful method for the construction of diquinanes of importance in the synthesis of sesquiterpene natural products. A number of alternatives to this reaction have been reported, involving various transition metals as catalysts or promoters.[2] We report herein the first known examples of iron carbonyl promoted cyclocarbonylations of 1,6-enynes to give bicyclo[3.3.0]octen-3-ones.[3]

Results and Discussion

General Methodology. A series of six enyne ethers were synthesized by standard methods using the Williamson reaction.[4] Cyclization of these substrates was attempted under a variety of reaction conditions to optimize the yields. Table 1 lists a series of bicyclooctenone ethers which have been prepared by the thermal $Fe(CO)_5$-promoted cyclization under CO pressure in acetonitrile as solvent. All the bicyclooctenones synthesized in this work are high-boiling oils which are readily purified by column chromatography. Billington[4] has reported yields of enones **8** and **12** to be 14% and 41%, respectively, using the Pauson–Khand reaction, which involved isolation and purification of a stable cobalt alkyne complex. No such intermediates can be isolated in our method, nor is isolation necessary. If the reactions are conducted at temperatures lower than about 120 °C, no reaction is observed. Cyclization of a terminal alkyne could not be effected with these ether derivatives but is successful in the case of all-carbon enynes (see below). Ito[5] has reported a Ni(0)-promoted cyclization of enyne **3** in the presence of phenyl isocyanide to give the imine derivative of **10**. While this reaction proceeds in good yield (62%), a separate hydrolysis step is required to yield the enone.

Table 1. $Fe(CO)_5$-Promoted Cyclization of Enyne Ethers to Oxabicyclo Enones in Acetonitrile



enyne	bicyclooctenone	temp (°C)	pressure (psig)	time (h)	yield (%)
1	**8**	135	60	35	0
2	**9**	135	60	21	50
3	**10**	140	55	26	77
4	**11**	135	55	64	46.5
5	**12**	142	55	44	22
7	**13**	135	60	40	0

An attempt to synthesize the 8-oxabicyclononenone **13** was unsuccessful and instead gave only a complex mixture of unidentifiable products. This is in contrast somewhat with previous work in our laboratories leading to syntheses of bicyclo[4.3.0]nonadienones by the $Fe(CO)_5$-promoted cyclization of 1,7-diynes, a more facile reaction than the present enyne cyclization, which leads to good yields of cyclization products.[6]

While several of these reactions do proceed in reasonably good yields, we searched for milder reaction conditions which might be tolerated by a sensitive functionality in the enyne substrate and give greater selectivity for the desired cyclization product. Since the cyclization reaction presumably involves the formation of a coordinatively unsaturated $Fe(CO)_4$ intermediate by thermal dissociation of a CO ligand from $Fe(CO)_5$, we sought other means of

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⊛ Abstract published in *Advance ACS Abstracts,* April 1, 1994.

[1] For a recent review, see: Schore, N. E. *Org. React.* **1991**, *40* (Chapter 1).

[2] Zirconium: Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568. Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336. Agnel, G.; Owczarczyk, Z.; Negishi, E. *Tetrahedron Lett.* **1992**, *33*, 1543. Titanium: Grossman, R. B.; Buchwald, S. L. *J. Org. Chem.* **1992**, *57*, 5803. Molybdenum: Mukai, C.; Uchiyama, M.; Hanaoka, M. *J. Chem. Soc., Chem. Commun.* **1992**, 1014. Rhodium: Doyama, K.; Joh, T.; Shiohara, T.; Takahashi, S. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 4354.

[3] Preliminary communication: Pearson, A. J.; Dubbert, R. A. *J. Chem. Soc., Chem. Commun.* **1991**, 202. Taken in part from the Ph.D. dissertation of R. A. Dubbert.

[4] Billington, D. C.; Willison, D. *Tetrahedron Lett.* **1984**, *25*, 4041.

[5] Tamao, K.; Kobayashi, K.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 1286.

[6] Shively, R. J., Jr. Ph.D. Dissertation, Case Western Reserve University, 1994. Pearson, A. J.; Shively, R. J., Jr.; Dubbert, R. A. *Organometallics* **1992**, *11*, 4096.

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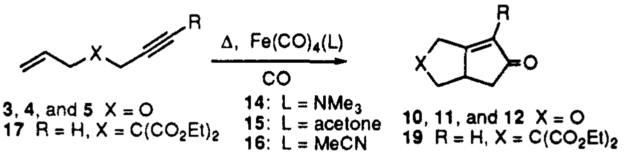
Table 2. Cyclizations Promoted by $Fe(CO)_4$(ligand) Complexes



enyne	$Fe(CO)_4L$	temp (°C)	pressure (psig)	time (h)	enone (yield (%))
3	**14**	100	35	10.6	**10** (36)
3	**15**	135	25	60	**10** (87)
4	**16**	135	75	23	**11** (76)
5	**15**	135	70	70	**12** (43)
5	**16**	130	60	32	**12** (47)
17	**15**	135	40	65	**19** (55)

Table 3. $Fe(CO)_5$-Promoted Cyclization of 3-Alkoxy 1,6-Enynes

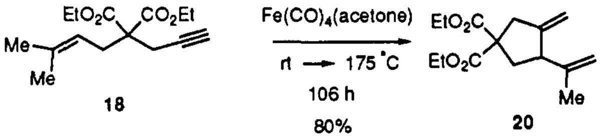
enyne	temp (°C)	CO pressure (psig)	time (h)	enone	total yield (%)	ratio **a**:**b**
21	140	80	52.2	**25**	27	1.9:1
22	125–154	75	112.5	**26**	20	13:1
23	145	75	30.1	**27**	48	5:1
24	140	75	44.4	**28**	45	5.2:1

generating this species under less severe reaction conditions. Irradiation with ultraviolet light will photodissociate CO from $Fe(CO)_5$, and several attempts were made to cyclize enyne **3** using a standard Hanovia UV lamp. A complex mixture of products was obtained, either from [2 + 2] cycloaddition reactions or further reactions of the product bicyclooctenone. Irradiation with a visible light source proved to be somewhat more successful, but this method was not found to be general for all enyne substrates and was not further pursued.

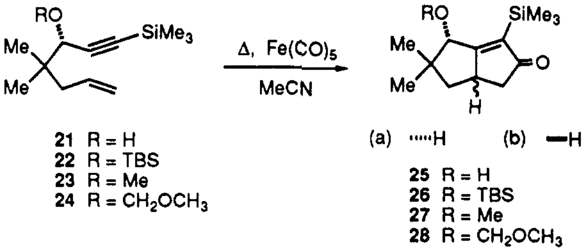
Cyclization of 1,6-enynes by $Fe_2(CO)_9$ in toluene was also attempted. Reaction of a 1,6-enyne with $Fe_2(CO)_9$ was expected to displace a carbonyl ligand to give the enyne complex $Fe(CO)_4$(enyne) and $Fe(CO)_5$ under mild conditions. However, no cyclization was observed at room temperature, and subsequent heating of the mixture gave mostly a complex mixture of unidentified products. Mild chemical methods also exist for displacement of CO from metal carbonyls. Amine oxides are well-known to react with metal carbonyls to displace carbon monoxide and are often used to disengage organic ligands from metal carbonyl complexes.[7] Reaction of $Fe(CO)_5$ with trimethylamine *N*-oxide at −50 °C in toluene gave a deep red solution presumably containing the amine–$Fe(CO)_4$ complex. Reaction of this mixture with enyne **3** gave a 36% yield of enone **10**. However, an attempted cyclization of enyne **17** gave a complex product mixture with only small amounts of enone. Owing to the poor reproducibility of this cyclization method, we attempted no further experiments and sought other means of chemically generating "$Fe(CO)_4$".

Another source of $Fe(CO)_4$ is from the reaction of acetone and $Fe_2(CO)_9$ to give a deep burgundy solution which presumably contains $Fe(CO)_4$(acetone) and $Fe(CO)_5$. The solvent and $Fe(CO)_5$ are readily removed by vacuum distillation to give a deep red air-sensitive solid which is assumed to be the acetone complex. This solid has not been completely characterized, and its stoichiometry is currently unknown. Our attempts to cyclize enyne **3** with $Fe_2(CO)_9$ in acetone as solvent gave only a complex mixture of products and black pyrophoric iron. However, $Fe(CO)_4$(acetone) in toluene promoted the cyclization of **3** to give **10** in 87% yield. An analogous complex may be prepared from acetonitrile and $Fe_2(CO)_9$ to give $Fe(CO)_4$(MeCN) (**16**). This complex is also a dark red highly air-sensitive material which has never been completely characterized. Enynes **4** and **5** were successfully cyclized using this reagent to give bicyclooctenones **11** and **12** in 76% and 47% yield, respectively. Table 2 lists results using these complexes to promote cyclization of enynes. Yields of cyclocarbonylation products are generally higher than those obtained using iron pentacarbonyl in acetonitrile, although the latter is operationally more convenient.

We have also investigated the feasibility of cyclizing 1,6-enyne esters **17** and **18**, which were easily synthesized by using standard methods. $Fe(CO)_4$(acetone)-promoted cyclization of **17** gave enone **19** in 55% yield (Table 2). The cyclization proceeds with a terminal alkyne, a reaction which was not possible in the case of enyne ether **1**. Attempted cyclization of enyne ester **18**, under all reaction conditions discussed above, gave no visible bicyclooctenone products but instead gave the ene product **20**. Repetition of this experiment under identical conditions in the absence of $Fe(CO)_4$(acetone) also gave the thermal ene product, but this was contaminated by other byproducts. The possibility that $Fe(CO)_4$(acetone) acts as a promoter for the ene reaction in this case was not investigated further and remains to be confirmed with other substrates. Trost[8] has reported carbocyclizations of 1,6-enynes to 1,4-dienes that are promoted by Pd(II) acetate complexes and proceed through a palladium hydride intermediate. A similar iron hydride intermediate could promote the ene reaction in our case.



$Fe(CO)_5$-Promoted Cyclization of 3-Alkoxy 1,6-Enynes. In order to study the diastereoselectivity of the $Fe(CO)_5$-promoted cyclization of enynes, we synthesized a series of 3-alkoxy-substituted enynes as described in the literature by Magnus[9] in his synthesis of coriolin and hirsutic acid. This gave us a direct comparison between the stereochemical outcome of the $Fe(CO)_5$-promoted cyclization versus the Pauson–Khand cyclization. These enynes represent a series of alkoxy-substituted derivatives ranging in steric demand from a hydroxyl to a bulky *tert*-butyldimethylsilyl group.



The stereochemical assignments of the bicyclooctenones summarized in Table 3 were made on the basis of their ^1H NMR spectra following Magnus' determination of the

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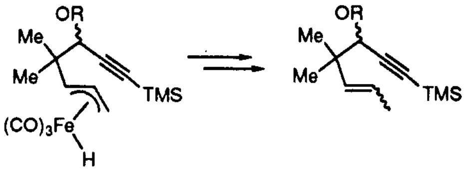
[7] Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1974**, 336. Shen, J. K.; Gao, Y. C.; Shi, Q. Z.; Basolo, F. *Organometallics* **1989**, *8*, 2144.

[8] Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1985**, *107*, 1781.

[9] Magnus, P.; Exon, C.; Albaugh-Robertson, P. *Tetrahedron* **1985**, *41*, 5861.

structure for **26**.[9] The ^{1}H NMR spectrum for **26** contains a singlet at 4.16 ppm for the proton geminal to the OTBS ($OSiMe_2$-*t*-Bu) group, while the minor diastereomer with the OTBS group on the β-face has a singlet at 4.72 ppm for the geminal proton. We have used this trend in chemical shifts in assigning structures to the diastereomers we observed. In the case of enone **26**, Magnus observed a diastereomeric ratio of 26:1 of **26a**:**26b** for the $Co_2(CO)_8$-promoted cyclization of **22**. We obtained a diastereomeric ratio of 12.7:1 for the $Fe(CO)_5$-promoted cyclization before chromatography of the products on silica gel. The ratio increases to 25:1 after column chromatography, indicating a significant amount of isomerization and/or fractionation. The Ni(0)-promoted cyclization of a similar 1,6-enyne has been reported to give a 10:1 ratio of diastereomers.[5]

A major byproduct observed in the crude ^{1}H NMR of the products from these reactions is the 5-en-1-yne isomer of the starting material. Isomerization of the double bond probably occurs through the iron hydride intermediate **29**, which effectively competes with cyclization to the bicyclooctenone. Apparently, this isomerization is essentially irreversible under our reaction conditions. We have so far been unable to overcome this problem; no improvement was observed when complexes **14**–**16** were used to effect the cyclization.



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In the cyclization of the 3-hydroxyenyne **21** to the 8-hydroxybicyclooctenone **25**, the diastereomeric ratio decreases to 1.9:1. A lower diastereomeric ratio would be expected due to the lower steric demand of a hydroxy versus a (*tert*-butyldimethylsilyl)oxy group. It is also interesting to note that we were able to cyclize an unprotected alcohol, a reaction that has been reported as being difficult for the Pauson–Khand reaction.[10] Although our yield of 27% is low, related cyclizations of 1,6-diyne alcohols proceed in excellent yields.[11] This is consistent with the general observation that diynes cyclize more readily than enynes under our reaction conditions. A major byproduct also isolated from the present reaction in 51% yield is the double-bond isomer of starting material.

Cyclization of 3-methoxy-1,6-enyne **23** to give the 8-methoxybicyclooctenone **27** gave a 5:1 mixture of diastereomers in 48% yield; apparently the methoxy group exhibits a greater steric influence than the hydroxy group. Also isolated in 19% yield was the double-bond isomer of the starting material. The methoxymethyl-protected enyne alcohol **24** was cyclized to bicyclooctenone **28** in 45% yield along with a 46% yield of the double-bond isomer of **24**. ^{1}H NMR of the products before chromatography showed mostly bicyclooctenone and the isomer. It is interesting to note that no double-bond isomerization was observed during the cyclizations of the enyne ethers **1**–**5**. Why cyclization occurs more readily with these substrates is still unknown. Yields of the carbocyclic enones were consistently lower than those of the oxabicyclooctenones.

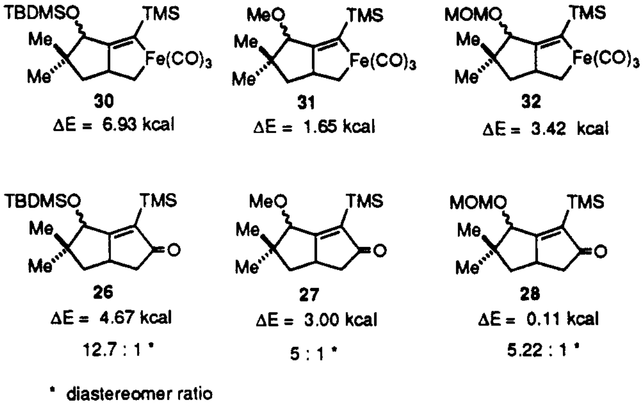

Figure 1.

We have performed MMX calculations (PC Model) to obtain the relative steric energies of diastereomeric 16-electron ferracyclopentene intermediates and product bicyclooctenones as depicted in Figure 1. The ferracyclopentenes pictured are crude approximations to the structure of the transition state for the initial cyclocoupling reaction where the diastereomeric product distribution is probably determined. Factors affecting the stability of these intermediates are likely to affect the transition state in a similar manner. The largest steric energy difference observed was for ferracyclopentene **30**, which also led to the largest diastereomeric ratio of bicyclooctenones. There is at least a *qualitative* correlation between the calculated steric energy differences and the diastereomeric ratios observed experimentally. The correlation is poorer when the energy differences between the final product diastereomers are used, suggesting that equilibration and thermodynamic control is not occurring.

Conclusions

We have demonstrated that $Fe(CO)_5$ will promote the cyclization of 1,6-enynes to bicyclooctenones in a manner similar to that of $Co_2(CO)_8$. Enyne ethers undergo cyclization most readily, with no apparent formation of isomerized alkenes. Enynes with alkoxy or silyloxy substituents at C-3 also undergo cyclization with modest to good diastereoselectivity, but in lower yields. Pregeneration of $Fe(CO)_4$ as $Fe(CO)_4(MeCN)$ or $Fe(CO)_4$(acetone) allows cyclocarbonylation in higher yield, but the reaction still requires a high temperature and also involves the synthesis and handling of air-sensitive intermediates.

Experimental Section

For a general description of experimental procedures and spectroscopic characterization, see ref 11.

Allyl Propargyl Ether (1). This compound was synthesized by the method of Billington.[4] To 50 mL of EtOH was added 6.90 g (123 mmol) of powdered KOH and 5.64 g (100.6 mmol) of propargyl alcohol. The mixture was stirred at 0 °C for 20 min; then 14.1 g (117 mmol) of allyl bromide was added dropwise. The mixture was stirred at room temperature for 34 h, 10 mL of H_2O was added, and the solution was extracted with ether. After removal of the solvent, the crude enyne was vacuum-distilled at 110 mmHg to give 4.30 g (44.8 mmol, 44.5% yield) of a major fraction boiling at 48 °C. ^{1}H NMR (300 MHz): δ 5.98–5.85 (m, 1H), 5.29 (2 d, $\Delta\nu$ = 28.3 Hz, J = 17.3 and 10.4 Hz, 2 H), 4.16 (d, J = 2.37 Hz, 2 H, propargylic CH_2), 4.07 (d, J = 5.8 Hz, 2 H, allylic CH_2), 2.44 (t, J = 2.37, 1 H, alkyne CH). Gas chromatography: retention time on a Supelcowax 10 column is 5.5 min using the temperature program described for compound **5**.

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(10) Rowley, E. G.; Schore, N. E. *J. Organomet. Chem.* **1991**, *413*, C5.

(11) Pearson, A. J.; Shively, R. J., Jr. *Organometallics* **1994**, *13*, 578.

Allyl 3-(Trimethylsilyl)prop-2-ynyl Ether (2). To 7.90 mL (0.012 mol) of *n*-BuLi in hexanes under Ar at −78 °C was added 1.11 g (11.6 mmol) of allyl propargyl ether in 20 mL of ether. After the mixture was stirred for 30 min, 1.37 g (12.6 mmol) of chlorotrimethylsilane in 10 mL of ether was added. The mixture was stirred at room temperature for 15 h, cooled to 0 °C, and quenched by addition of 5 mL of water. The organic layer was separated, and the aqueous layer was extracted with ether. The combined ether layers were dried over $MgSO_4$. The solvent was removed by distillation. Vacuum distillation of the residue at 30 mmHg gave 1.06 g (6.32 mmol, 54.5% yield) of a major fraction boiling at 89 °C. ^1H NMR (300 MHz): δ 6.0–5.86 (m, 1H, vinyl CH), 5.36–5.20 (m, 2H, vinyl CH_2), 4.16 (s, 2H, propargylic CH_2), 4.08 (d, J = 5.7 Hz, 2H, allylic CH_2), 0.20 (s, 9H, $SiMe_3$). Gas chromatography: retention time 7.64 min using the temperature program described for compound **5**.

Allyl 3-Phenylprop-2-ynyl Ether (3). The ether was prepared by the method of Bartlett.[12] To 25 mL of THF under N_2 at room temperature was added 2.10 g (87.5 mmol) of NaH and 8.42 g (64 mmol) of 3-phenylprop-2-yn-1-ol purchased from Farchan Laboratories and used without further purification. The mixture was stirred overnight at 50 °C. Then 9.38 g (78 mmol) of allyl bromide was added and the mixture further stirred for 24 h at 50 °C. The mixture was poured into 18 mL of water and extracted with a total of 135 mL of diethyl ether. The ether was dried over $MgSO_4$, and the solvent was removed under vacuum. Vacuum distillation of the residue at 0.05 mmHg gave 8.73 g (50.7 mmol, 79.3% yield) of a major fraction boiling at 63 °C. ^1H NMR (300 MHz): δ 7.45–7.26 (m, 5H, phenyl), 6.0–5.87 (m, 1H, vinylic CH), 5.36–5.19 (m, 2H, vinylic CH_2), 4.35 (s, 2H, propargylic CH_2), 4.10 (d, J = 5.7 Hz, allylic CH_2). ^{13}C NMR (75 MHz): δ 134, 131, 128.3, 128, 122, 118, 86, 85, 70, 58.

Allyl Pent-2-ynyl Ether (4). To 45 mL of THF under Ar at 0 °C was added 1.38 g (57.5 mmol) of NaH. Then 3.98 g (47.2 mmol) of 2-pentyn-1-ol was added dropwise, and the mixture was stirred overnight at room temperature. Then 7.00 g (57.8 mmol) of allyl bromide was added dropwise. The mixture was stirred for 2 days at room temperature and then for 10 h at 55 °C; 3.0 mL of water was then added followed by 40 mL of ether. The ether layer was washed with 6 × 10 mL of water, and the H_2O washings were extracted with 2 × 10 mL of ether. The ether was removed by distillation at 1 atm. The residue was distilled at 30 mmHg to give 3.49 g (28.1 mmol, 57.9% yield) of a major fraction boiling at 60 °C. ^1H NMR (300 MHz): δ 5.93–5.80 (m, 1H), 5.28–5.13 (m, 2H), 4.07 (t, J = 1.9 Hz, alkynyl $-OCH_2$), 3.99 (d, J = 5.8 Hz, 2H, allylic CH_2), 2.22–2.14 (quartet of triplets, J = 7.5 and 1.9 Hz, ethyl CH_2), 1.10 (t, J = 7.5 Hz). ^{13}C NMR (75 MHz): δ 134.1, 117.4, 88.1, 74.9, 70.2, 57.5, 13.6, 12.3. Gas chromatography: retention time for the compound is 7.81 min using the temperature program described for compound **5**.

Allyl But-2-ynyl Ether (5). The compound was synthesized by the method of Bartlett.[12] To 1.05 g (43.8 mmol) of NaH powder in 30 mL of THF at 0 °C was added 2.68 g (38.3 mmol) of 2-butyn-1-ol dropwise. The mixture was stirred for 12 h at room temperature. A white solid precipitated, and 30 mL of THF was added. Then 5.25 g (74.6 mmol) of allyl bromide was slowly added and the mixture stirred for 24 h at room temperature. The mixture was quenched with 5 mL of water and extracted with ether. After removal of ether by distillation, the residue was vacuum-distilled at 30 mmHg to give 2.46 g (22.4 mmol, 58.4% yield) of a major fraction boiling at 45–50 °C. ^1H NMR (300 MHz): δ 5.91–5.78 (m, 1H, H-2), 5.27–5.12 (m, 2H, H-1), 4.04 (s, 2H, propargylic CH_2), 3.98 (d, J = 5.7 Hz, 2H, allylic CH_2), 1.80 (s, 3H, Me). ^{13}C NMR (75 MHz): δ 134, 117.3, 82.2, 74.8, 70.2, 57.5, 3.31. Gas chromatography: retention time for the compound on a Supelcowax 10 column is 7.16 min using the temperature program 100 °C initial temperature, hold for 5 min, increase temperature 5 °C/min up to 220 °C, and then hold for 20 min.

3-Butenyl Propargyl Ether (6). To 10 mL of THF at 0 °C under N_2 was added 1.77 g (24.5 mmol) of 3-buten-1-ol. Then 2.77 g (23.3 mmol) of propargyl bromide (80 wt % in toluene) in 5 mL of THF was added dropwise over a period of 4 h with slow addition of 1.44 g (25.7 mmol) of solid KOH. A mixture of a yellow-orange solution and white solid resulted and was warmed to room temperature. After extractive workup with ether/water, the ether and THF were removed by distillation at 1 atm to give an orange residue. Vacuum distillation of the residues at 35 mmHg gave 1.28 g (11.6 mmol, 47.5% yield) of a major fraction boiling at 55 °C. ^1H NMR (300 MHz): δ 5.88–5.76 (m, 1H, vinyl CH), 5.18–5.04 (m, 2H, vinyl CH_2), 4.15 (d, J = 2.4 Hz, 2H), 3.59 (t, J = 6.7 Hz, 2H), 2.43 (t, J = 2.4 Hz, 1H), 2.42–2.32 (m, 2H).

3-Butenyl 3-(Trimethylsilyl)prop-2-ynyl Ether (7). To 10 mL of THF at −75 °C under N_2 were added 798.2 mg (7.25 mmol) of enyne **6** and 5.45 mL (8.72 mmol) of 1.6 M *n*-BuLi in hexanes. After the mixture was stirred for 1 h at −75 °C, 1.28 g (11.8 mmol) of chlorotrimethylsilane in 3 mL of THF was added dropwise. The solution turned colorless, and a white solid precipitated. The mixture was slowly warmed to room temperature overnight. TLC analysis of the mixture (9:1 hexanes/EtOAc) showed a major spot at R_f 0.78. The mixture was cooled to 0 °C, and 3 mL of H_2O was added. The layers were separated, and 10 mL of ether was added. The organic layer was washed with 2 × 3 mL of H_2O, and the H_2O washings were extracted with 5 mL of ether. The combined ether extracts were washed with saturated $NaHCO_3$, followed by 3 mL of saturated NaCl, and then dried over $MgSO_4$. The solvent was removed by distillation at 1 atm. The crude product was purified by flash chromatography on a 5$^3/_4$ in. × 40 mm column of silica gel with 9:1 hexanes/EtOAc as eluent. The solvent was removed by distillation at 1 atm to give 493.1 mg (2.71 mmol, 37.4% yield) of the enyne, which contained unidentified minor impurities. ^1H NMR (300 MHz): δ 5.88–5.7 (m, 1 H), 5.15–5.03 (m, 2 H), 4.15 (s, 2 H, propargylic CH_2), 3.58 (t, J = 6.7 Hz, 2 H), 2.37 (m, 2 H), 0.19 (s, 12 H, $SiMe_3$). ^{13}C NMR (75 MHz): δ 134.9, 116.4, 101.5, 91.1, 69.2, 58.8, 33.9, 0.23.

2-(Trimethylsilyl)-7-oxabicyclo[3.3.0]octen-3-one (9). To 8 mL of MeCN were added 127.9 mg (0.76 mmol) of allyl 3-(trimethylsilyl)prop-2-ynyl ether (**2**) and 197.5 mg (0.94 mmol) of $Fe(CO)_4(MeCN)$, which was prepared as described below. The mixture was heated to 135 °C at 60 psig of CO for 21.2 h. GC analysis of the products showed only a small amount of starting material remaining. The solvent was removed under vacuum to give a brown residue. The crude product was eluted through a column of neutral alumina with $CHCl_3$. The solvent was removed under vacuum to give 75.1 mg (0.38 mmol, 50% yield) of a yellow oil, which was found to be the bicyclooctenone. IR ($CHCl_3$): 1696.6, 1612 cm^{-1}. ^1H NMR (300 MHz): δ 4.58 (AB q, $\Delta\nu_{AB}$ = 52.5 Hz, J_{AB} = 16.2 Hz, 2H, H-8), 4.33 (s, 1H, H-6), 3.23–3.22 (m, 2H, H-5 and H-6), 2.66–2.58 (dd, J = 17.3 and 5.7 Hz, 1H, H-4), 2.15–2.08 (dd, J = 17.3 and 3.4 Hz, 1H, H-4), 0.20 (s, 9H, $SiMe_3$). Gas chromatography: retention time on a Supelcowax 10 column was 25.5 min using the above temperature program.

2-Phenyl-7-oxabicyclo[3.3.0]octen-3-one (10). To 7 mL of MeCN in a Fisher–Porter pressure reaction vessel were added 287.6 mg (1.47 mmol) of $Fe(CO)_5$ and 124 mg (0.72 mmol) of allyl 3-phenylprop-2-ynyl ether (**3**). The mixture was freeze–pump–thawed three times, pressurized to 55 psig of CO, and heated to 140 °C (70 psig CO) for 26 h. The resulting orange solution was reduced to an orange oil under vacuum. The crude products were eluted through a 4$^1/_4$ in. × 38 mm silica gel flash column with ether. Fractions containing a UV-active spot at R_f 0.43 were combined, and the solvent was removed under vacuum to give 110.8 mg (0.55 mmol, 77%) of an orange oil. IR ($CHCl_3$): 3018, 1707, 1663 cm^{-1}. ^1H NMR (300 MHz): δ 7.54–7.32 (m, 5H, phenyl), 4.75 (AB q, $\Delta\nu_{AB}$ = 105 Hz, J_{AB} = 16.4 Hz, 2H), 4.37 (t, J = 7.3 Hz, 1H), 3.32 (m, 1H), 3.25–3.19 (dd, J = 7.3 and 4.1 Hz, 1H), 2.87–2.79 (dd, J = 17.6 and 6.1 Hz, 1H), 2.36–2.29 (dd, J = 17.6 and 6.1 Hz, 1H). ^{13}C NMR (75 MHz): δ 206.7, 177.3, 134.5, 130.5, 128.5, 127.9, 71.2, 66.2, 43.2, 40.2, 0.00. HRMS: m/z (M^+) calcd 200.083 72, found 200.0846.

2-Ethyl-7-oxabicyclo[3.3.0]octen-3-one (11). To 8 mL of MeCN in a glass prv were added 116.3 mg (0.94 mmol) of allyl pent-2-ynyl ether (4) and 349 mg (1.78 mmol) of $Fe(CO)_5$. The

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[12] Bartlett, A. J.; Laird, T.; Ollis, W. D. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1315.

solution was freeze–pump–thawed three times and pressurized to 55 psig of CO. It was heated to 135 °C for 64.1 h at 70 psig of CO. The solution was cooled, and the solvent was removed in vacuo to give a black oil. The crude product was purified on a 5 in. × 38 mm silica gel column with 4:1 hexanes/EtOAc as eluent. Fractions containing a UV-active spot at R_f 0.15 were combined and the solvent removed to give 66.2 mg (0.435 mmol, 46.5% yield) of a yellow oil. IR ($CHCl_3$): 1711, 1672 cm^{-1}. ^1H NMR (300 MHz): δ 4.61 (AB q, $\Delta\nu_{AB}$ = 28.4 Hz, J_{AB} = 15.6 Hz, 2H), 4.34–4.31 (m, 1H), 3.24–3.19 (m, 2H), 2.72–2.64 (dd, J = 17.7 and 5.85 Hz, 1H), 2.34–2.19 (m, 2H, ethyl -CH_2), 2.17–2.10 (dd, J = 17.79 and 2.41 Hz, 1H), 1.12–1.07 (t, J = 7.62 Hz, 3H, Me). ^{13}C NMR (75 MHz): δ 208.8, 175.5, 138.2, 71.7, 64.8, 43.5, 38.9, 17.6, 12.2. HRMS: m/z (M^+) calcd 152.083 72, found 152.0839. Gas chromatography: retention time 25.7 min on a Supelcowax 10 column using the temperature program described above.

A procedure for preparation of the above compound using $Fe(CO)_4(MeCN)$ is as follows. To 8 mL of toluene were added 202.5 mg (0.97 mmol) of $Fe(CO)_4(MeCN)$ and 99.1 mg (0.80 mmol) of enyne **4**. The prv was pressurized to 55 psig of CO and heated to 135 °C for 22.8 h at 70 psig of CO. GC analysis of the products showed complete conversion of the starting material. The solvent was removed under vacuum to give a brown oil. Purification of the crude products on alumina, with $CHCl_3$ as eluent, gave 92.1 mg (0.61 mmol, 76% yield) of **11**.

2-Methyl-7-oxabicyclo[3.3.0]octen-3-one (12). To 8 mL of MeCN in a glass prv were added 121.7 mg (1.11 mmol) of allyl but-2-ynyl ether (**5**) and 432.8 mg (2.21 mmol) of $Fe(CO)_5$. The solution was freeze–pump–thawed three times and pressurized to 55 psig of CO. It was heated to 142 °C (70 psig of CO) for 43.75 h. After the mixture was cooled to room temperature, the solvent was removed in vacuo to give a black oil. The crude products were purified on a 4 in. × 38 mm silica gel column with neat ether as eluent. Fractions containing a UV-active spot at R_f 0.31 were combined and the solvent removed to give 33.3 mg (0.241 mmol, 21.7%) of a yellow oil. IR ($CHCl_3$): 1713, 1680 cm^{-1}. ^1H NMR (300 MHz): δ 4.54 (AB q, $\Delta\nu_{AB}$ = 33 Hz, J_{AB} = 15.4 Hz, 2H), 4.32–4.30 (m, 1H), 3.23–3.19 (m, 2H), 2.71–2.64 (dd, J = 17.9 and 5.56 Hz, 1H), 2.17–2.09 (dd, J = 18 and 2.10 Hz, 1H), 1.77 (s, 3H, Me). ^{13}C NMR (75 MHz): δ 209.03, 176.12, 132.55, 71.81, 64.68, 43.16, 38.63, 8.95. HRMS: m/z (M^+) calcd 138.068 07, found 138.0678. Gas chromatography: retention time on a Supelcowax 10 column was 24.9 min using the above temperature program.

A procedure for the preparation of the above compound using $Fe(CO)_4(MeCN)$ is as follows. To 7 mL of MeCN were added 186.1 mg (0.89 mmol) of $Fe(CO)_4(MeCN)$ prepared as described below and 93.2 mg (0.85 mmol) of enyne **5**. The prv was pressurized to 45 psig of CO and the mixture heated to 130 °C. After 32.4 h a GC analysis of the products showed complete conversion of the enyne. The solvent was removed under vacuum to give a brown oil. The crude products were purified by elution through a 4.3-cm column of neutral alumina with $CHCl_3$ as eluent to give 55.3 mg (0.4 mmol, 47.3% yield) of bicyclooctenone.

A procedure for the preparation of the above compound using $Fe(CO)_4$(acetone) is as follows. To 8 mL of degassed toluene were added 206.4 mg (0.914 mmol) of $Fe(CO)_4$(acetone) and 116.1 mg (1.05 mmol) of enyne **5**. The prv was pressurized to 60 psig of CO and heated to 135 °C at 80 psig of CO. After 69.5 h GC analysis of the mixture showed almost complete conversion of the starting material. The solvent was removed under vacuum to give a brown oil. The crude products were purified by passage through a column of neutral alumina with $CHCl_3$. Removal of the solvent gave 62.2 mg (0.45 mmol, 43% yield) of **12**.

$Fe(CO)_4$(acetone) (15). A typical preparation of this compound is as follows. To 10 mL of acetone which had been degassed by freeze–pump–thawing was added 709.5 mg (1.95 mmol) of $Fe_2(CO)_9$. The mixture was stirred for 5 h at room temperature to give a deep red solution. The solvent was removed under vacuum to give a yellow distillate and 206.4 mg (0.91 mmol) of a deep red solid residue. Solutions of the solid decomposed within minutes when exposed to air.

$Fe(CO)_4(MeCN)$ (16). A typical preparation of this compound is as follows. To 10 mL of MeCN which had been degassed by three freeze–pump–thaw cycles was added 760.5 mg (2.09 mmol) of $Fe_2(CO)_9$ under N_2. The mixture was stirred for 5 h at room temperature to give a deep red solution. The solvent was removed under vacuum to give a yellow distillate and 197.5 mg (0.95 mmol, 45.2% yield) of a deep red solid residue. Solutions of the solid decomposed within minutes when exposed to air.

Diethyl Allylpropargylmalonate (17). To 0.29 g (12.6 mmol) of Na dissolved in 30 mL of ethanol was added 2.56 g (12.9 mmol) of diethyl propargylmalonate (prepared by the method of Dötz[13]) at 0 °C with vigorous stirring. After 20 min 1.97 g (16.3 mmol) of allyl bromide was added dropwise. The solution was stirred for 12 h at room temperature until no further reaction was observed by gas chromatographic analysis of the products. The solvent was removed under vacuum and the residue vacuum-distilled to give 1.19 g (5.0 mmol, 39% yield) of diethyl allylpropargylmalonate. IR (neat): 1740 cm^{-1}. ^1H NMR (400 MHz): δ 5.70–5.60 (m, 1H), 5.23–5.14 (m, 2H), 4.25–4.20 (q, J = 7.1 Hz, 4H, ester CH_2), 2.84–2.78 (m, 4H), 2.04–2.03 (t, J = 2.7 Hz), 1.29–1.26 (t, J = 7.1 Hz, ester CH_3). ^{13}C NMR (75 MHz): δ 169.4, 131.5, 119.5, 78.6, 61.4, 56.3, 36.1, 22.3, 13.8.

7-Methyl-4,4-bis(ethoxycarbonyl)oct-6-en-1-yne (18). To 40 mL of EtOH was added 0.44 g (19.1 mmol) of Na at 0 °C. Then 2.93 g (14.8 mmol) of diethyl propargylmalonate was added. The solution was stirred for 20 min, and then 15.3 mL of a MeCN solution of 4-bromo-2-methyl-2-butene (15.3 mmol) was added dropwise over 15 min at 0 °C. The solution was slowly warmed to room temperature. It was stirred for 18 h, and then another 1.0 mL of the MeCN solution of 4-bromo-2-methyl-2-butene (1 mmol) was added. The solution was stirred another 24 h, and the volume was reduced under vacuum. The residue was dissolved in 25 mL of ether, washed with 2 × 8 mL of H_2O followed by 5 mL of saturated aqueous NaCl, and dried over $MgSO_4$. The solution was then reduced to an oil under 0.05 mmHg. The yield of the enyne was 1.90 g (7.12 mmol, 47.5%). ^1H NMR (400 MHz): δ 4.93 (t, J = 1.3 Hz, 1H), 4.27–4.17 (q, J = 7.1 Hz, 4H ester CH_2), 2.80–2.79 (m, 4H), 2.0 (t, J = 2.6 Hz, 1H), 1.71 and 1.67 (2 s, 3 H each, 2 × Me), 1.26 (t, J = 7.1 Hz, 6H, ester Me).

7,7-Bis(ethoxycarbonyl)bicyclo[3.3.0]octen-3-one (19). To 8 mL of toluene in a glass prv were added 131.3 mg (0.581 mmol) of $Fe(CO)_4$(acetone) and 114.2 mg (0.48 mmol) of diethyl allylpropargylmalonate. The prv was pressurized to 40 psig of CO and heated to 135 °C (55 psig of CO) for 65 h. The solvent was removed under vacuum to give a brown oil. Purification of the crude products by chromatography on neutral alumina with $CHCl_3$ as eluent gave 103.9 mg (0.39 mmol, 81% yield) of the bicyclooctenone containing unidentified impurities. No further purification of this compound was attempted. ^1H NMR (400 MHz): δ 5.96 (s, 1 H), 4.30–4.16 (m, 4H, ester CH_2), 3.40–3.25 (AB q, $\Delta\nu_{AB}$ = 39.2 Hz, J_{AB} = 18.9 Hz, 2H), 3.13 (m, 1H), 2.85–2.79 (dd, J = 12.7 and 7.6 Hz, 1H), 2.68–2.62 (dd, J = 17.9 and 6.3 Hz, 1H), 2.18–2.12 (dd, J = 17.9 and 3.2 Hz, 1H), 1.79–1.73 (m, 1H), 1.32–1.26 (m, 6H, ester Me).

1-(Trimethylsilyl)-3-hydroxy-4,4-dimethylhept-6-en-1-yne (21). To 80 mL of hexane under Ar at 0 °C was added 16 mL (24.8 mmol) of 1.55 M n-BuLi in hexanes. Then 2.51 g (25.6 mmol) of (trimethylsilyl)acetylene was added dropwise. A white solid precipitated. The mixture was stirred at room temperature for 6 h. Then 2.89 g (25.78 mmol) of 2,2-dimethyl-4-pentenal was added at 0 °C. Most of the white solid dissolved. The solution was stirred at room temperature for 12 h and then at 50 °C for 1 h. The mixture was cooled to 0 °C, and 10 mL of water was added. The hexane layer was washed with two more 10-mL portions of water, the water washings were extracted with 2 × 20 mL portions of ether, and the combined ether extracts were dried over $MgSO_4$ overnight. The solvent was removed by distillation at atmospheric pressure, and the residue was vacuum distilled at 5 mmHg to give 4.48 g (21.3 mmol, 83.2% yield) of a major fraction boiling at 80–90 °C. ^1H NMR (300 MHz): δ 5.91–5.77 (m, 1H), 5.11–5.04 (m, 2H), 4.04 (d, J = 6.0 Hz, 1H), 2.21–2.06 (m, 2H), 1.90 (d, J = 6.0 Hz, 1H, -OH), 0.97 and 0.96

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[13] Dötz, K. H.; Popall, M. *Tetrahedron* **1985**, *41*, 5797.

(2 s, 3 H each, 2 × Me), 0.18 (s, 9H, $-SiMe_3$). ^{13}C NMR (75 MHz): δ 134.9, 117.6, 105.4, 90.6, 70.5, 42.7, 38.6, 22.6, 22.5, 0.00. HRMS: *m/z* ($M^+ - CH_3$) calcd 195.120 51, found 195.12045. No M^+ was observed.

1-(Trimethylsilyl)-3-(methoxymethoxy)-4,4-dimethylhept-6-en-1-yne (24). To 25 mL of THF under N_2 at −70 °C were added 1.63 g (16.6 mmol) of (trimethylsilyl)acetylene and 5.90 mL (14.8 mmol) of 2.5 M *n*-BuLi in hexanes. The solution was slowly warmed to −50 °C over 1 h and then cooled to −70 °C, and 1.51 g (13.4 mmol) of 2,2-dimethyl-4-pentenal was added. This solution was slowly warmed to 0 °C and stirred for 3.5 h. The mixture was cooled to −50 °C, and 3.81 g (47.30 mmol) of chloromethyl methyl ether was added. After it was stirred at room temperature for 15 min, the mixture was refluxed for 3 h. TLC analysis of the products (9:1 hexanes/EtOAc) showed a major spot at R_f 0.58. The volume of the mixture was reduced about 50% and cooled to 0 °C; then 5 mL of H_2O was added, followed by 30 mL of ether. The ether layer was washed with 2 × 5 mL of H_2O and the aqueous washings extracted with 2 × 10 mL of ether. The combined ether extracts were washed with 5 mL of saturated NaCl and dried over Na_2SO_4. The solvent was removed in vacuo to give a yellow liquid. The crude products were purified by flash chromatography on a $5^1/_4$ in. × 3 in. wide silica gel column with 9:1 hexanes/EtOAc as eluent. Fractions containing a spot at R_f 0.60 were combined, and the solvent was removed in vacuo to give 2.40 g (9.4 mmol, 70% yield) of product. ^{1}H NMR (300 MHz): δ 5.90–5.76 (m, 1H), 5.08–5.02 (m, 2H, C-7), 4.97 (d, *J* = 6.7 Hz, 1H, OCH_2O), 4.57 (d, *J* = 6.7 Hz, 1H, OCH_2O), 4.01 (s, 1H, C-3), 3.39 (s, 3H, OCH_3), 2.23–2.09 (m, 2H), 0.99 (s, 3H), 0.98 (s, 3H), 0.17 (s, 9H, $SiMe_3$). ^{13}C NMR (75 MHz): δ 134.9, 117.5, 103.0, 94.4, 91.5, 73.8, 55.8, 43.0, 37.9, 23.1, 22.8, 0.00.

8-Hydroxy-7,7-dimethyl-2-(trimethylsilyl)bicyclo[3.3.0]-octen-3-one (25). To 8 mL of MeCN were added 349.0 mg (1.78 mmol) of $Fe(CO)_5$ and 147.0 mg (0.70 mmol) of heptenyne **21**. The mixture was freeze–pump–thawed three times and pressurized to 80 psig of CO. The solution was heated to 140 °C for a total of 52.2 h at 90 psig of CO. The solution was cooled and the solvent removed under vacuum to give a brown oil. TLC analysis (1:1 hexanes/EtOAc) showed spots at R_f 0.74, 0.44, and 0.36. Flash chromatography of the crude products on a $4^1/_2$ in. × 38 mm column of silica gel with 1:1 hexanes/EtOAc as eluent gave 45.1 mg (0.189 mmol, 27.1% yield) of an oil identified as a mixture of bicyclooctenone diastereomers with R_f 0.44 and 0.36. Also found were 75.1 mg (0.36 mmol, 51.1% yield) of an oil identified as the double-bond isomer of the starting material. No further attempt was made to separate the diastereomers. IR ($CHCl_3$): 3019, 2958, 1685, 1610 cm^{-1}. ^{1}H NMR (300 MHz; mixture): δ 4.40 (d, *J* = 6.0 Hz, H-8 minor), 4.30 (s, H-8 major, total of 1H for both diastereomers), 3.30–3.40 (m, H-5 major), 2.95–3.04 (m, H-5 minor, total 1H for both diastereomers), 2.58–2.71 (overlapping dd, *J* = 17.6 and 6.9 Hz for major, H-5, total of 1H for both diastereomers), 1.85–2.10 (m, H-4 and H-6, total of 3H for both diastereomers), 0.96–1.31 (m, Me's and H-6, total of 7H for both diastereomers), 0.25 (2 s, $SiMe_3$, total of 9H for both diastereomers). ^{13}C NMR (75 MHz): δ 214.9, 213.8, 199.1, 194.4, 139.2, 138.4, 78.0, 77.2, 45.3, 45, 44.4, 44.1, 43.9, 43.3, 43.2, 43.1, 42.7, 42.6, 29.3, 28.2, 23.8, 22.9, 0.0. HRMS: *m/z* (M^+) calcd 238.1389, found 238.1383.

8-((*tert*-Butyldimethylsilyl)oxy)-7,7-dimethyl-2-(trimethylsilyl)bicyclo[3.3.0]octen-3-one (26). To 8 mL of MeCN were added 205.1 mg of heptenyne **22** (0.63 mmol) and 447 mg (2.28 mmol) of $Fe(CO)_5$. The mixture was freeze–pump–thawed three times and pressurized to 75 psig of CO. The mixture was heated to 125 °C for 19.2 h at 90 psig of CO. A ^{1}H NMR spectrum of the mixture showed that the conversion of the starting material was very low. The temperature was increased to 135 °C for 22.8 h, at which time the conversion of the starting material was still low. The temperature was raised to 145 °C for a further 23.2 h and then to 154 °C for 47.3 h in order to get complete conversion of the starting material. When conversion was complete, the mixture was cooled and the solvent was removed under vacuum to give a brown oil. TLC of the crude products (9:1 hexanes/EtOAc) gave two spots at R_f 0.68 and 0.31. The crude products were purified by flash chromatography on a $4^3/_4$ in. × 40 mm silica gel column with 9:1 hexanes/EtOAc as eluent. Fractions containing spots at R_f 0.31 were combined to give 43.6 mg (0.124 mmol, 19.6% yield) of an oil. The compound was characterized by ^{1}H NMR as a diastereomeric mixture of bicyclooctenones by comparison with ^{1}H NMR data reported by Magnus.[9] IR ($CHCl_3$): 2956, 2931, 1685, 1653 cm^{-1}. ^{1}H NMR (300 MHz): δ 4.18 (s, 1H), 3.34–3.44 (m, 1H), 2.69 (dd, *J* = 17.8 and 7.11 Hz, 1H), 2.08–1.96 (m, 2H), 1.14 (s, 3H). ^{13}C NMR (75 MHz): δ 216.7, 195.0, 136.1, 77.4, 46.1, 44.1, 42.2, 42.1, 28.5, 25.7, 24.1, 18.2, 0.0. The structural assignment of the diastereomers was made on the basis of the H-8 proton chemical shift as reported by Magnus[9] for the crude products before chromatography. The proton geminal to the OTBS group has a δ 4.16 ppm for the major diastereomer and δ 4.76 for the minor one. We found a diastereomeric ratio of about 12.7:1 before chromatography on silica gel and 25:1 after, indicating some fractionation or isomerization of the product.

7,7-Dimethyl-8-methoxy-2-(trimethylsilyl)bicyclo[3.3.0]-octen-3-one (27). To 8 mL of MeCN were added 197.1 mg (0.879 mmol) of heptenyne **23** and 475.1 mg (2.43 mmol) of $Fe(CO)_5$. The mixture was freeze–pump–thawed three times and pressurized to 55 psig of CO. The mixture was heated at 145 °C (75 psig CO) for a total of 30.1 h, at which time ^{1}H NMR of the mixture showed almost complete conversion of starting material. The mixture was cooled and solvent removed under vacuum. TLC analysis (9:1 hexanes/EtOAc) of the crude products showed spots at R_f 0.56, 0.33, and 0.23. The crude product was purified by flash chromatography on a 5 in. × 40 mm silica gel column with 9:1 hexanes/EtOAc as eluent. Fractions containing spots at R_f 0.56 were combined to give 37.9 mg (0.17 mmol, 19.2% yield) of an oil identified by ^{1}H NMR as the double-bond isomer of **23**. Fractions containing spots at R_f 0.33 and 0.23 were combined to give 106.7 mg (0.423 mmol, 48.1% yield) of an oil identified by ^{1}H NMR as a mixture of the two diastereomeric bicyclooctenones.

Major diastereomer: IR ($CHCl_3$) 2957, 1696, 1616 cm^{-1}; ^{1}H NMR δ 3.82 (s, 1H, H-8), 3.30 (s, 3H, OMe), 3.29–3.21 (m, 1H, H-5), 2.70–2.62 (d, *J* = 17.7 and 7.0 Hz, 1H, H-4), 2.04–1.95 (m, 2H, H-4 and H-6), 1.15 (s, 3H, Me), 0.84 (s, 3H, Me), 0.22 (s, 9H, $SiMe_3$); ^{13}C NMR (75 MHz) δ 214.9, 193.4, 139.8, 85.4, 57.1, 45.8, 43.4, 42.8, 42.5, 29.6, 23.3, 0.0; HRMS *m/z* (M^+) calcd 252.1545, found 252.1537.

1-(Trimethylsilyl)-3-methoxy-4,4-dimethylhept-5-en-1-yne byproduct: ^{1}H NMR (300 MHz) δ 5.60–5.42 (m, 2H, H-2 and H-3), 3.54 (s, 1H, H-5), 3.40 (s, 3H, OMe), 1.69 (d, *J* = 6.0 Hz, 3H), 1.07 (s, 6H, 2 × Me), 0.19 (s, 9H, $SiMe_3$).

1-(Trimethylsilyl)-3-(methoxymethoxy)-4,4-dimethylhept-5-en-1-yne byproduct: ^{1}H NMR (300 MHz) δ 5.55–5.49 (m, 2H, vinylic CH), 4.95 (d, *J* = 6.8 Hz, 1H, OMOM CH_2), 4.55 (d, *J* = 6.8 Hz, 1H, OMOM CH_2), 4.0 (s, 1H, H-8), 3.37 (s, 3H, OMOM CH_3), 1.70 (dd, *J* = 6 and 1 Hz, vinyl CH_3), 1.1 (s, 6H, 2 × Me), 0.17 (s, 9H, $SiMe_3$).

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research (Grant No. CHE 93-08105). R.A.D. thanks BP America for a leave of absence, during which time this work was undertaken.

OM930892U