JOC Article

2,5-Dialkyl Cyclohexenones by $Fe(CO)_5$-Mediated Carbonylation of Alkenyl Cyclopropanes: Functional Group Compatibility

Douglass F. Taber,* Pramod V. Joshi, and Kazuo Kanai

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

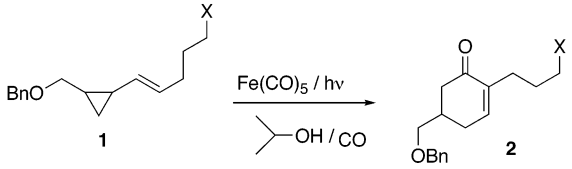
taberdf@udel.edu

Received August 29, 2003

The preparation of alkenyl cyclopropanes **1** with a variety of common organic functionalities is reported. These substrates were subjected to the $Fe(CO)_5$-mediated carbonylation process under a CO atmosphere, leading to the formation of 2,5-disubstituted cyclohexenones **2**, important intermediates for target-directed synthesis.

Introduction

We recently reported[1a] a general method for the construction of 5-alkyl cyclohexenones[2] by UV irradiation of alkenyl cyclopropanes **1** in the presence of $Fe(CO)_5$ under a CO atmosphere.[3] The ease of preparation of the enantiomerically pure alkenyl cyclopropanes used in this process enables the rapid construction of cyclohexane derivatives. This reaction enables the rapid assembly of 2,5-disubstituted cyclohexenone derivatives, which are suitable intermediates for target-directed synthesis.[4] We report here a preliminary investigation of the compatibility of this procedure with common organic functional groups.



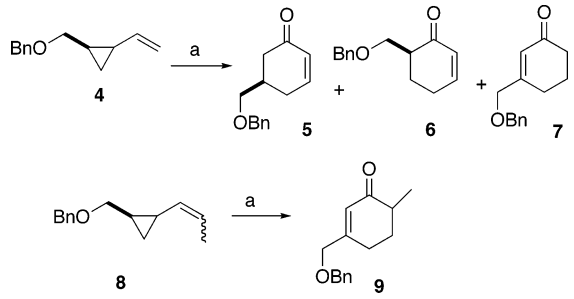
(1) (a) Taber, D. F.; Kanai, K.; Jiang, Q.; Bui, G. *J. Am. Chem. Soc.* **2000**, *122*, 6807. (b) Sarel, S. *Acc. Chem. Res.* **1978**, *11*, 204. (c) Khusnutdinov, R. I.; Dzhemilev, U. M. *J. Organomet. Chem.* **1994**, *471*, 1. (d) Schulze, M. M.; Gockel, U. *Tetrahedron Lett.* **1996**, *37*, 357. (e) Schulze, M. M.; Gockel, U. *J. Organomet. Chem.* **1996**, *525*, 155.

(2) For alternate approaches to 5-alkyl cyclohexenones, see: (a) Asaoka, M.; Shima, K.; Takei, H. *Tetrahedron Lett.* **1987**, *28*, 5669. (b) Schwarz, J. B.; Devine, P. N.; Meyers, A. I. *Tetrahedron* **1997**, *53*, 8795. (c) Hareau, G. P.-J.; Koiwa, M.; Hikichi, S.; Sato, F. *J. Am. Chem. Soc.* **1999**, *121*, 3640. (d) Sarakinos, G.; Corey, E. J. *Org. Lett.* **1999**, *1*, 811.

(3) (a) Davies, H. M. L.; Bruzinski, P. R.; Lake, D. H.; Kong, N.; Fall, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 6897. (b) Zhou, S.-M.; Deng, M.-Z.; Xia, L.-J. *Angew. Chem., Int. Ed.* **1998**, *37*, 2845. (c) Lo, M. M.-C.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 10270. (d) Charette, A. B.; Juteau, H.; Lebel, H.; Molinaro, C. *J. Am. Chem. Soc.* **1998**, *120*, 11943. (e) Schwartz, J. B.; Meyers, A. I. *J. Org. Chem.* **1998**, *63*, 1619. (f) Temme, O.; Taj, S.-A.; Andersson, P. G. *J. Org. Chem.* **1998**, *63*, 6007. (g) Fox, M. E.; Li, C.; Marino, J. P., Jr.; Overman, L. E. *J. Am. Chem. Soc.* **1999**, *121*, 5467.

(4) For examples of the importance of 2,5-dialkyl cyclohexenones in natural product synthesis, see: (a) Ohshima, T.; Xu, Y.; Takita, R.; Shimizu, S.; Zhong, D.; Shibasaki, M. *J. Am. Chem. Soc.* **2002**, *124*, 14546. (b) Armstrong, A.; Davies, N. G. M.; Martin, N. G.; Rutherford, A. P. *Tetrahedron Lett.* **2003**, *44*, 3915. (c) Corminboeuf, O.; Overman, L. E.; Pennington, L. D. *J. Am. Chem. Soc.* **2003**, *125*, 6650.

SCHEME 1[a]



[a] Conditions: (a) $Fe(CO)_5$, *hν*, benzene; DBU.

Results and Discussion

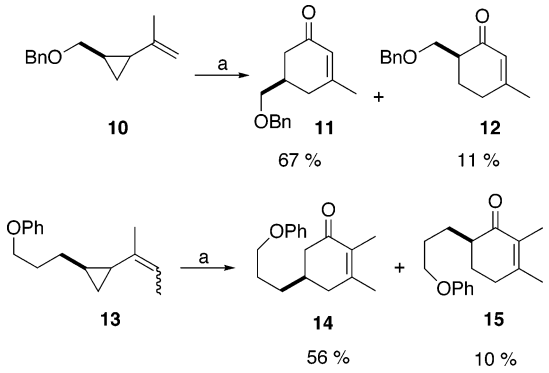
Establishment of the Reaction. Fe-mediated carbonyl insertion across a vinyl cyclopropane system to generate the corresponding cyclohexenone was first reported by Sarel and co-workers.[1b] Their study aimed at establishing whether vinyl cyclopropanes could provide a ligand of four π electrons for metal coordination. This early work did not address the regio- and stereochemical issues arising from such a carbonyl insertion.

We initally[1a] focused on the vinyl cyclopropane **4** (Scheme 1). We observed three regioisomers from the photochemically initiated $Fe(CO)_5$ carbonylation. Thus, UV irradiation (Scheme 1) with $Fe(CO)_5$ in benzene followed by treament with DBU converted cyclopropane **4** mainly to the 5-alkyl cyclohexenone **5**, the desired regioisomer. We also observed the regioisomer **6** and the alkene-migrated enone **7**. While the enone **7** was a minor product from the Fe-mediated carbonylation of **4**, the corresponding enone **9** was the dominant product from the Fe-mediated carbonylation of **8**. We concluded that **7** was formed by "Fe−H" isomerization of **4**, and we tried several additives to suppress this unwanted alkene migration. We eventually found that running the reaction in *2-propanol* minimized the formation of the isomerized byproducts **7** and **9**.

Our preliminary exploration of the scope of this cyclocarbonylation is shown in Scheme 2. Disubstituted

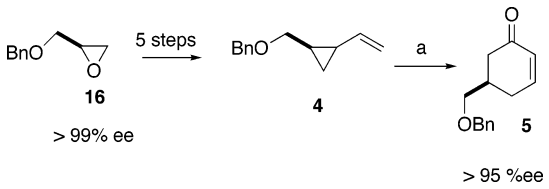
10.1021/jo0302760 CCC: $27.50 © 2004 American Chemical Society
Published on Web 02/28/2004

SCHEME 2[a]



[a] Conditions: (a) Fe(CO)$_5$, *hν*, benzene; DBU.

SCHEME 3[a]



[a] Conditions: (a) Fe(CO)$_5$, *hν*, 2-propanol; DBU.

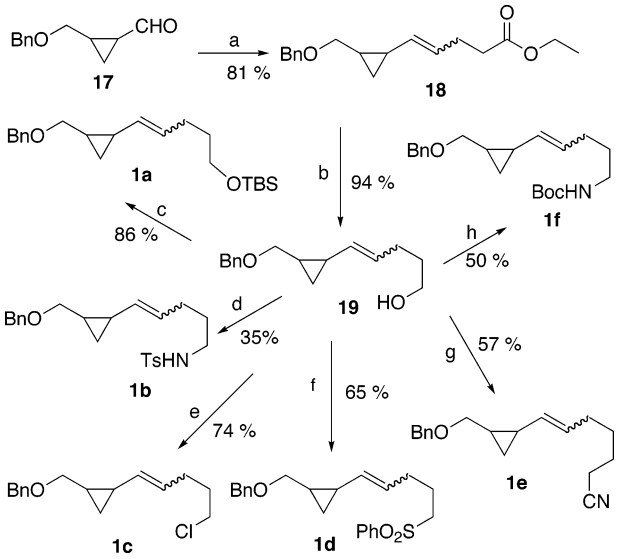
alkenes participated efficiently, while the yield of the cyclohexenones was lower with trisubstituted alkenes. Since the starting alkenyl cyclopropanes were mixtures of *Z*- and *E*-isomers, we subjected each of the isomers separately to the Fe-mediated process and found that each participated efficiently.

The issue of absolute stereocontrol was addressed by preparing the enantiomerically pure cyclopropane **4** from the commercially available enantiomerically pure epoxide **16**. The product cyclohexenone **5** was shown to be >95% ee by chiral HPLC anaylsis (Scheme 3). Thus, no racemization occurred during the Fe-mediated carbonylation process. All other alkenyl cyclopropanes in the work described here were racemic.

Functional Group Compatibility. Wittig homologation[5] (Scheme 4) of the aldehyde **17**[1a] gave the ester **18**. Reduction of ester **18** with lithium aluminum hydride gave the key intermediate, alcohol **19**. The alcohol **19** was protected under standard conditions to give **1a**. Mitsunobu[6a,b] reaction of **19** gave the azide which was converted to sulfonamide **1b** and Boc-amine **1f**. Chlorination of alcohol **19** with NCS[6c] gave the chloro cyclopropane **1c**. Tosylation of **19** followed by sulfone displacement[6d] gave **1d**, and cyanide displacement[6e] of the benzenesulfonate of **19** gave cyclopropane **1e**.

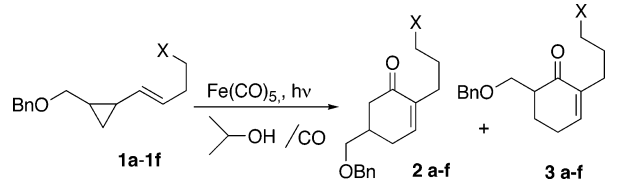
The substrates **1a**−**f** were subjected to the photochemically initiated Fe(CO)$_5$ carbonylation process under one atmosphere of CO pressure in Pyrex tubes in a Rayonet apparatus (350 nm) at ambient temperature. All of the reactions were run in 2-propanol to minimize the

SCHEME 4[a]



[a] Conditions: (a) KO^{t}Bu, Ph$_3$P(CH$_2$)$_3$CO$_2$Et; (b) LAH, THF, 0 °C; (c) TBDMSCl, TEA, DMAP, CH$_2$Cl$_2$; (d) (1) Ph$_3$P, DIAD, THF, (2) LAH, THF, (3) TsCl, TEA, DMAP, CH$_2$Cl$_2$; (e) NCS, Ph$_3$P; (f) (1) TsCl, TEA, DMAP, CH$_2$Cl$_2$, (2) NaSO$_2$Ph, THF; (g) (1) BsCl, TEA, DMAP, CH$_2$Cl$_2$, (2) KCN, DMF−H$_2$O; (h) (1) Ph$_3$P, DIAD, THF, (2) LAH, THF, (3) Boc$_2$O, TEA, DMAP, CH$_2$Cl$_2$.

TABLE 1. Results of Photolysis of Alkenyl Cyclopropanes



entry	X	2/3	yield (%)
1	(a) OTBS	5.9:1	80
2	(b) NHTs	5.2:1	75
3	(c) Cl	6.3:1	68
4	(d) SO_2Ph	4.7:1	68
5	(e) CN	4.2:1	66
6	(f) NHBoc	3.4:1	72

formation of the isomerized byproducts. At the end of the irradiation, we found it convenient to add DBU[1a] to convert the intermediate products to the more stable conjugated isomers (Table 1).

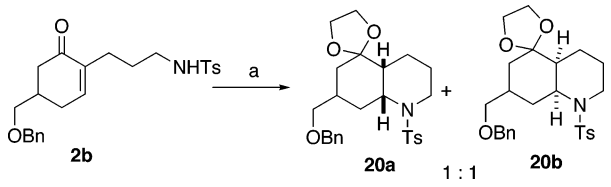
Limitations of the Carbonylation Process. An alkenyl cyclopropane bearing a free alcohol (X= OH, **19**) underwent several competing oxido-reductive processes along with the desired cyclocarbonylation diminishing its synthetic utility (yield of enone **2g** = 34%). The free thio group (X = SPh) similarly underwent competing oxidation reactions, making it incompatible with this process (yield of enone **2h** = 26%). Cyclopropane **1** with a ketone (X = $COCH_3$) gave alkene migration to conjugate the double bond with the ketone as a competing side reaction (yield of enone **2i** = 24%). Ester **18** similarly gave the desired cyclohexenone **2j** along with the product of migration to conjugate the alkene with the ester (yield of enone **2j** = 27%).

Cyclopropane **1** with a bromo functionality (X = Br) seemed to participate efficiently in the carbonylation

(5) (a) Schimdt, U.; Leiberknecht, A.; Griesser, H.; Utz, R.; Beuttler, T. F., Barknoviah, F. *Synthesis* **1986**, 361. (b) Danheiser, R. L.; Halgason, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 9471.

(6) (a) Mitunobu, O. *Synthesis* **1981**, 1. (b) Hughes, D. L. *Org. Prep. Proc. Int.* **1996**, *28*, 127. (c) Sugimoto, O.; Mori, M.; Tanji, K.-i. *Tetrahedron Lett.* **1999**, *40*, 7477. (d) Taber, D. F.; Yu, H. *J. Org. Chem.* **1997**, *62*, 1687. (e) Taber, D. F.; Song, Y. *J. Org. Chem. Soc.* **1997**, *62*, 6603.

SCHEME 5[a]



[a] Conditions: (a) $CH(OEt)_3$, *p*-TsOH, $(CH_2OH)_2$.

process, but DBU treatment after the photolysis led to partial elimination of the bromide (yield of enone **2k** = 21%, yield of allyl enone = 7%). Cyclopropane diene **1** (X = CH_2) was not a suitable substrate, as it gave a complex mixture of alkenes, apparently resulting from double bond migration under carbonylation conditions.

Preparation of an Azabicyclic Core. When cyclohexenone **2b** (X = NHTs) was treated[7]with ethylene glycol, triethyl orthoformate, and *p*-toluenesulfonic acid to protect the ketone as the ketal, we received instead the cis-fused decahydroquinoline **20** as a 1:1 mixture of diastereomers. These interesting cis-fused ring structures represent the core of several alkaloids such as pumiliotoxin C[8] and the lepadins (Scheme 5).[9]

Conclusion. The $Fe(CO)_5$-mediated carbonylation of alkenyl cyclopropanes described here appears to be a general method for the construction of 5-alkyl cyclohexenone derivatives. The process is tolerant of a variety of common functional groups, which enhances the complexity of the cyclohexenones generated by this method. The product 2,5-disubstituted cyclohexenones are key building blocks for target directed synthesis.[4]

Experimental Section[10]

Ester 18. To potassium *tert*-butoxide (2.5 g, 0.022 mol) in 40 mL of THF was added phosphonium salt (10.2 g, 0.022 mol) in three portions over 5 min. The reaction mixture was stirred at 0 °C for 2 h and at room temperature for 15 min. The reaction mixture was cooled back to 0 °C, and then aldehyde **17** (3.26 g, 0.017 mol) in 30 mL of THF was added dropwise and the reaction mixture was stirred from 0 to 10 °C over 2 h. The mixture was partitioned between MTBE and, sequentially, 0.5 M aqueous HCl and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to give 4.02 g (81% yield) of the ester **18** as a clear oil. TLC: R_f = 0.37 (10% MTBE/PE). ^{1}H NMR δ: 7.26−7.35 (5 H, m); 5.29 (1 H, dt, J = 7.1, 9.9 Hz); 4.85 (1 H, t, J = 9.9 Hz); 4.55 (2 H, s); 4.13 (2 H, q, J = 7.1 Hz); 3.34 (1 H, dd, J = 3.4, 6.8 Hz); 3.33 (1 H, dd, J = 3.4, 6.8 Hz); 2.48 (2 H, m); 2.39 (2 H, m); 1.47 (1 H, m); 1.13 (1 H, m); 1.25 (3 H, t, J = 7.1 Hz); 0.71 (1 H, m); 0.61 (1 H, m). ^{13} C NMR δ d: 14.3, 15.2, 20.4, 126.4, 127.6, 127.7, 128.4, 133.7, u: 12.4, 23.2, 34.4, 60.3, 72.6, 73.4, 138.5, 173.2. IR: 1730, 1449, 1176 cm^{-1}. MS (*m*/*z*): 288 (M^+), 214, 181 (100), 121. HRMS: calcd for $C_{18}H_{24}O_3$ 288.1725, found 288.1717. Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.95; H, 8.39. Found: C, 74.80; H, 8.55.

Alcohol 19. To ester **18** (1.43 g, 4.9 mmol) in 16 mL of THF at 0 °C was added LAH (376 mg, 9.9 mmol) in three portions. The reaction mixture was stirred at 0 °C for 40 min (TLC control). The mixture was partitioned between MTBE and, sequentially, 0.5 M aqueous HCl and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to give 1.11 g (91% yield) of alcohol **19** as a clear oil. TLC: R_f = 0.17 (25% MTBE/PE). ^{1}H NMR δ: 7.27−7.35 (5 H, m); 5.30 (1 H, m); 4.88 (1 H, ddd, J = 1.2, 2.5, 10.8 Hz); 4.54 (2 H, s); 3.60 (2 H, m); 3.21 (1 H, dd, J = 2.2, 10.1 Hz); 2.41−2.43 (1 H, m); 2.20 (2 H, m); 1.72 (2 H, m); 1.57 (2 H, m); 1.12 (1 H, m); 0.68 (1 H, dt, J = 4.9, 8.4 Hz); 0.61 (1 H, dt, J = 4.9, 8.4 Hz). ^{13}C NMR δ d: 16.2, 20.2, 127.7, 127.9, 128.5, 130.6, 133.1, u: 12.3, 23.7, 32.1, 61.4, 72.6, 73.7, 138.2. IR: 3408, 1452, 1070 cm^{-1}. MS (*m*/*z*): 246 (M^+), 169, 139 (100), 129, 121. HRMS: calcd for $C_{16}H_{22}O_2$ 246.1619, found 246.1609.

TBS Ether 1a. To alcohol **19** (502 mg, 2.0 mmol) in 7 mL of CH_2Cl_2 at 0 °C were added sequentially imidazole (417 mg, 6.1 mmol), DMAP (37.4 mg, 0.31 mmol), and TBSCl (615 mg, 4.1 mmol). The reaction mixture was stirred from 0 °C to room temperature over 12 h. The mixture was partitioned between MTBE and, sequentially, aqueous saturated $NaHCO_3$ and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to give 630 mg (86% yield) of the TBS ether **1a** as an oil. TLC: R_f = 0.87 (5% MTBE/PE). ^{1}H NMR δ: 7.31 (5 H, m); 5.33 (1 H, dt, J = 7.5, 10.6 Hz); 4.83 (1 H, t, J = 10.6 Hz); 4.51 (2 H, d, J = 3.2 Hz); 3.62 (2 H, t, J = 6.7 Hz); 3.30 (1 H, dd, J = 3.1, 10.6 Hz); 2.19 (2 H, m); 1.67 (2 H, m); 1.48 (1 H, m); 1.1 (1 H, m); 0.91 (9 H, s); 0.71 (1 H, dt, J = 5.0, 8.4 Hz); 0.67 (1 H, m); 0.05 (6 H, s). ^{13}C NMR δ d: 5.1, 15.9, 18.5, 26.1, 127.7, 127.8, 128.5, 128.7, 132.7, u: 12.6, 18.5, 24, 33.1, 62.8, 72.6, 73.6, 138.7. IR: 2852, 1255, 1100 cm^{-1}. MS (*m*/*z*): 360 (M^+),195, 141, 91(100). HRMS: (M+ H) calcd for $C_{22}H_{37}O_2Si$ 361.2563, found 361.2556.

Sulfonamide 1b. To DPPA[6a] (1.5 g, 5.5 mmol) in 7 mL of THF at 0 °C was added DEAD (951 mg, 5.5 mmol) over 2 min. The reaction mixture was stirred for 10 min, and then a premixed 10 mL THF solution of alcohol **19** (1.12 g, 4.6 mmol) and Ph_3P (1.31 g, 5.0 mmol) was added over 5 min. The reaction mixture was stirred from 0 °C to room temperature over 2 h. The mixture was partitioned between MTBE and, sequentially, aqueous saturated NH_4Cl and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to give 780 mg of the azide. TLC: R_f = 0.58 (7% MTBE/PE).

To the azide (909 mg, 3.4 mmol) in 11 mL of THF at 0 °C was added $LiAlH_4$[6b] (190 mg, 5.0 mmol). The reaction mixture was stirred over 2 h after which time 2 mL of methanol was added over 15 min. The resulting solid was filtered through a pad of Celite, and the solvent was removed. The residue was dissolved in 9 mL of CH_2Cl_2 and treated with triethylamine (441 mg, 4.4 mmol), DMAP (123 mg, 1 mmol), and *p*-toluenesulfonyl chloride (767 mg, 4 mmol) at room temperature for 12 h. The mixture was partitioned between CH_2Cl_2 and, sequentially, 1 M aqueous NaOH and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to give 1.02 g (35% yield from **19**) of sulfonamide **1b** as an light yellow oil. TLC: R_f = 0.43, 0.35 (30% MTBE/PE). ^{1}H NMR δ: 7.7 (2 H, d, J = 8.3 Hz); 7.26−7.34 (5 H, m); 5.21 (1 H, dt, J = 7.6, 10.6 Hz); 4.86 (2 H, m); 4.54 (2 H, d, J = 5.2 Hz); 3.45 (1 H, dd, J = 3.9, 10.2 Hz); 3.27 (1 H, dd, J = 2.8, 10.2 Hz); 2.92 (2 H, m); 2.41 (3 H, s); 2.22 (1 H, m); 2.14 (1 H, m); 1.60 (2 H, m); 1.45 (2 H, m); 0.67 (1 H, dt, J = 4.9, 8.4 Hz); 0.57 (1 H, m). ^{13} C NMR δ d: 16.2, 20.5, 21.7, 127.2, 127.4, 127.8, 127.9, 128.6, 129.8, 133.7, u: 12.4, 24.6, 29.4, 42.6, 72.7, 73.7, 137.2, 138.5, 143.4. IR: 3280,-1326, 1091 cm^{-1}. MS (*m*/*z*): 399 (M^+), 281, 261, 207, 139, 106 (100), 91. HRMS: calcd for $C_{23}H_{30}O_3NS$ (M + H) 400.1960, found 400.1946.

Chloride 1c. To alcohol **19** (497 mg, 2.0 mmol) in 6.7 mL of CH_2Cl_2 at 0 °C was added triphenylphosphine (809 mg, 3.1 mmol), followed by *N*-chlorosuccinimide[6c] (404 mg, 3.0 mmol). The reaction mixture was stirred from 0 °C to room temperature over 1.5 h. The solvent was removed, and the residue was chromatographed to give 428 mg (74% yield) of the chloride **1c**. TLC: R_f = 0.28 (5% MTBE/PE). ^{1}H NMR δ: 7.27−

(7) Back, T. G.; Nakajima, K. *J. Org. Chem.* **1998**, *63*, 6566.
(8) Ozawa, T.; Aoyagi, S.; Kibayashi, C. *J. Org. Chem.* **2001**, *66*, 3338.
(9) (a) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923. (b) Taber, D. F. *J. Org. Chem.* **1982**, *47*, 1351.
(10) For general experimental procedures, see the Supporting Information.

7.36 (5 H, m); 5.4 (1 H, m); 5.11 (1 H, t, J = 10.1 Hz); 3.57 (2 H, t, J = 6.6 Hz); 3.41 (1 H, m); 2.33 (2 H, m); 1.82 (2 H, m); 1.74 (1 H, m); 1.39 (1 H, m); 1.05 (1 H, ddd, J = 4.7, 8.3, 13.0 Hz); 0.62 (1 H, m); 0.35 (1 H, t, J = 5.4 Hz). ^{13}C NMR δ d: 14.2, 18.1, 128.5, 127.7, 127.9, 130.1, 133.8, u: 12.4, 24.8, 32.5, 44.7, 70.5, 72.7, 138.6. IR: 2931, 1450, 1095 cm^{-1}. MS (*m*/*z*): 264 (M$^+$), 233, 183 (100), 173. HRMS: calcd for $C_{16}H_{21}OCl$ 264.1281, found 264.1280.

Sulfone 1d. To alcohol **19** (665 mg, 2.7 mmol) in 9 mL of CH_2Cl_2 at 0 °C were added triethylamine (602 mg, 5.9 mmol), DMAP (66 mg, 0.5 mmol), and *p*-toluenesulfonyl chloride (618 mg, 3.2 mmol). The reaction mixture was stirred from 0 °C to room temperature over 12 h. The mixture was partitioned between CH_2Cl_2 and, sequentially, 1 M aqueous NaOH and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to give 863 mg of tosylate. TLC: R_f = 0.42 (25% MTBE/PE).

To the tosylate (645 mg, 1.6 mmol) in 5 mL of THF were added Bu_4NI (2.99 g, 8.1 mmol), Cu powder (16 mg, catalytic), and $PhSO_2Na$[6d] (826 mg, 5 mmol). The reaction mixture was refluxed for 12 h, cooled to room temperature, and diluted with 5 mL of H_2O. The mixture was partitioned between CH_2Cl_2 and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to give 650 mg (65% yield from **19**) of sulfone **1d** as an oil. TLC: R_f = 0.43, 0.38 (40% MTBE/PE). ^{1}H NMR δ: 7.9 (2 H, d, J = 7.8 Hz); 7.65 (1 H, m); 7.56 (2 H, t, J = 7.1 Hz); 7.26−7.37 (5 H, m); 5.18 (1 H, dt, J = 7.4, 10.7 Hz); 4.87 (1 H, t, J = 9.7 Hz); 4.52 (2 H, m); 3.4(2 H, m); 3.11 (2 H, m); 2.26 (2 H, m); 1.81 (2 H, m); 1.6 (1 H, m); 1.11 (1 H, m); 0.71 (1 H, dt, J = 4.9, 8.4 Hz); 0.59 (1 H, m). ^{13}C NMR δ d: 15.5, 20.2, 127.2, 127.3, 127.7, 128, 129, 133.4, 134.1, u: 12.1, 22.4, 25.6, 55.2, 72.1, 72.4, 138.3, 138.9. IR: 1447, 1309,1087 cm^{-1}. MS (*m*/*z*): 370 (M$^+$), 279, 169, 120 (100). HRMS: calcd for $C_{22}H_{26}O_3S$ 370.1603, found 370.1602.

Nitrile 1e. To alcohol **19** (620 mg, 2.5 mmol) in 8 mL of CH_2Cl_2 were added pyridine (332 mg, 3.3 mmol) and DMAP (62 mg, 0.5 mmol), followed by benzenesulfonyl chloride (534 mg, 3 mmol). The reaction mixture was stirred for 12 h at room temperature. The mixture was partitioned between CH_2Cl_2 and, sequentially, 1 M aqueous NaOH and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to give 930 mg (96%) of the benzenesulfonate. TLC: R_f = 0.27 (15% MTBE/PE).

To 756 mg (1.9 mmol) of the benzenesulfonate in 7.8 mL of 3:1 DMF/H_2O mixture was added KCN (1.2 g, 9.8 mmol). The reaction mixture was maintained at reflux for 12 h, cooled to room temperature, and diluted with 5 mL of H_2O. The mixture was partitioned between MTBE and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to give 285 mg (57% yield from **19**) of nitrile **1e** as an oil. TLC: R_f = 0.85 (36% MTBE/PE). ^{1}H NMR δ: 7.26−7.38 (5 H, m); 5.25 (1 H, dt, J = 7.5, 10.5 Hz); 4.94 (1 H, t, J = 10.5 Hz); 4.53 (2 H, s); 3.4(2 H, d, J = 6.8 Hz); 2.34 (4 H, m); 1.76 (2 H, m); 1.46 (1 H, m); 1.15 (1 H, m); 0.71 (1 H, m); 0.63 (1 H, dt, J = 4.7, 8,4 Hz). ^{13}C NMR δ d: 15.9, 20.6, 125.7, 127.7, 127.8, 128.5, 134.8, u: 12.5, 16.4, 25.5, 26.4, 72.6, 73.4, 119.9, 138.5. IR: 2244, 1447, 1068 cm^{-1}. MS (*m*/*z*): 255 (M$^+$), 164, 134, 120 (100). HRMS: calcd for $C_{17}H_{21}ON$ 255.1623, found 255.1617.

Boc-amine 1f. The amine (prepared as in **1b**) was dissolved in in 3.5 mL of CH_2Cl_2 and treated with triethylamine (117 mg, 1.2 mmol), DMAP (34 mg, 0.23 mmol), and di-*tert*-butyl dicarbonate (218 mg, 1.0 mmol) at room temperature for 12 h. The mixture was partitioned between CH_2Cl_2 and, sequentially, 1 M aqueous NaOH and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to give 209 mg (50% yield from **19**) of Boc-amine **1f** as an oil. TLC: R_f = 0.76, 0.72 (30% MTBE/PE). ^{1}H NMR δ: 7.27−7.39 (5 H, m); 5.31 (1 H, dt, J = 7.5, 10.6 Hz); 4.86 (1 H, t, J = 10.6 Hz); 4.72 (1 H, d, J = 5.9 Hz); 4.54 (2 H, d, J = 4.3 Hz); 3.40 (2 H, m); 3.13 (2 H, m); 2.21 (2 H, m); 1.57 (3 H, m); 1.44 (9 H, s); 1.12 (1 H, m); 0.7 (1 H, m); 0.6 (1 H, m). ^{13}C NMR δ d: 14.5, 20.7, 28.9, 127.9, 128.1, 128.2, 128.8, 133.4, u: 12.8, 25.2, 30.2, 40.5, 42.4, 72.9, 73.9, 138.9, 156.4. IR:1713, 1513, 1365 cm^{-1}. MS (*m*/*z*): 346 (M$^+$), 246, 169. HRMS: calcd for $C_{21}H_{32}O_3N$ 346.2381, found 346.2382

Representative Procedure for Fe(CO)$_5$ Carbonylation Process. To alkenyl cyclopropane **1a** (320 mg, 0.89 mmol) in 14 mL of 2-propanol (0.06 M) was added $Fe(CO)_5$ (359 mg, 1.8 mmol). The reaction vessel was purged with CO, a CO balloon was attached, and the mixture was photolyzed for 12 h at room temperature in a Rayonet apparatus (350 nm). At the end of irradiation, DBU (271 mg, 1.8 mmol) was added, and the mixture was stirred at room temperature for 1 h under nitrogen. The mixture was then partitioned between CH_2Cl_2 and, sequentially, 1 M aqueous HCl and brine. The combined organic extract was dried (Na_2SO_4) and concentrated. The residue was chromatographed to give 64.2 mg of unreacted **1a**, 190 mg of **2a,** and 31.8 mg of **3a**. TLC (8% MTBE/PE): **1a** R_f = 0.75, **2a** R_f = 0.37, and **3a** R_f = 0.49.

Cyclohexenone 2a. ^{1}H NMR δ: 7.27−7.38 (5 H, m); 6.71 (1 H, d, J = 2.9 Hz); 4.52 (2 H, s); 3.59 (2 H, t, J = 6.5 Hz); 3.42 (2 H, dd, J = 2.0, 5.6 Hz); 2.46−2.57 (2 H, m); 2.41 (1 H, m); 2.2−2.31 (2 H, m); 1.57−1.64 (2 H, m); 0.89 (9 H, s); 0.048 (6 H, s). ^{13} C NMR δ d: −5.1, 26.1, 36, 127.7, 127.8, 128.6, 144.3, u 18.5, 25.9, 29.4, 31.7, 41.7, 62.8, 73.3, 73.5, 138.4, 139.4, 199.2. IR:1674, 1249, 1095 cm^{-1}. MS (*m*/*z*): 331, 225, 191, 91 (100). HRMS: calcd for $C_{19}H_{27}O_3Si$ (M − C_4H_9) 331.1728, found 331.1729.

Cyclohexenone 3a. ^{1}H NMR δ: 7.27−7.35 (5 H, m); 6.71 (1 H, s); 4.54 (2 H, s); 3.87 (1 H, dd, J = 4.3, 9.5 Hz); 3.6 (3 H, m); 2.61 (1 H, m); 2.39 (2 H, m); 1.62 (2 H, m); 0.89 (9 H, s); 0.05 (6 H, s). ^{13} C NMR δ d: 5.1, 26.6, 47.5, 127.7, 127.8, 128.6, 145.2, u: 18.5, 25.4, 26.1, 26.2, 31.7, 62.9, 69.6, 73.4, 138.6, 139.3, 199.6. IR: 1667, 1251, 835 cm^{-1}. MS (*m*/*z*): 389 (M + H$^+$), 331, 223,105, 91 (100). HRMS: calcd for $C_{23}H_{37}O_3Si$ (M + H) 389.2495, found 389.2512.

Decahydroquinoline 20. To sulfonamide **2b** (100 mg, 0.23 mmol) in 1.2 mL of diethyl ether was added ethylene glycol (74 mg, 1.2 mmol) followed by *p*-toluenesulfonic acid (5.7 mg, 0.03 mmol) and triethyl orthoformate (100 mg, 0.68 mmol). The reaction mixture was stirred at room temperature for 2 h. The solvent was removed, and the residue was chromatographed to give 67.9 mg (62%) of ketals **20a** and **20b** (^{1}H NMR ratio ~1:1). TLC: R_f = 0.27 (30% MTBE/PE). The solid **20** was recrystallized from a CH_2Cl_2−PE mixture to give crystals suitable for X-ray structure determination, still in a 1:1 ratio. Mp: 97−98 °C. ^{1}H NMR δ: 7.72 (2 H, d, J = 8.3 Hz); 7.67 (2 H, d, J = 8.3 Hz); 7.35−7.38 (4 H, m); 7.24−7.33 (9 H, m); 7.13 (2 H, d, J = 8.3 Hz); 4.56 (2 H, q, J = 11.7 Hz); 4.46 (2 H, m); 4.31−4.39 (1 H, m); 4.26−4.3 (1 H, m); 3.82−3.94 (7 H, m); 3.82−3.84 92 H, m); 3.56−3.75 (2 H, m); 3.28 (2 H, d, J = 5.8 Hz); 2.92 (2 H, q, J = 13.6 Hz); 2.38 (6 H, d, J = 19.9 Hz); 2.15(1 H, m); 2.01 (1 H, m); 1.72−1.8 (3 H, m); 1.64−1.69 (4 H, m); 1.5−1.59 (5 H, m); 1.34−1.49 (6 H, m). ^{13} C NMR δ d: 21.6, 21.7, 32.5, 33.4, 43.4, 43.9, 49.7, 52.7, 127.1, 127.5, 127.6, 127.6, 127.8, 128.4, 128.5, 129.7, u: 20.3, 20.6, 22.2, 24.6, 24.9, 26.2, 30.7, 33.3, 40.1, 40.5, 64.1, 64.4, 64.5, 64.6, 72.4, 72.9, 73.3, 74.5, 110.2, 110.3, 138.5, 138.6, 138.7, 138.9, 142.9, 143.0. IR (KBr): 1337, 1151, 1093 cm^{-1}. MS (*m*/*z*,): 266, 222 (100), 197. HRMS: calcd for $C_{21}H_{34}O_3N$ (M + H) 472.2178, found 472.2158.

Acknowledgment. We thank the NIH (GM 60287) for support of this work. We thank Drs. Q. Jiang and B. Chen and undergraduates G. Bui and S. Patel for their contributions to the Fe-mediated carbonylation project. We thank John Dykins for acquiring MS data.

Supporting Information Available: Spectral data for cyclohexenones **2b**−**f**, and **3b**−**f**; characterization data (^{1}H NMR and ^{13} C NMR spectra) for alkenyl cyclopropanes **1a**−**f** and cyclohexenones **2a**−**f**, **3a**−**f**, and **20a** + **20b**; and X-ray structure of **20a** + **20b**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0302760