thentic sample. As the NMR data in the literature are incomplete, we recorded ^1H and ^{13}C NMR spectra in $CDCl_3$ and DMSO-d_6 at 270 MHz. The signals were assigned by ^1H-^1H and ^1H-^{13}C-COSY measurements.

5: mp 223 °C; $[\alpha]^{20}_D = -64.9°$ (*c* 1, MeOH);[8e,40] ^1H NMR ($CDCl_3$) δ 0.88 (d, J = 7.0 Hz, 3 H, 12-CH_3), 0.93 (t, J = 7.3 Hz, 3 H, 13-CH_2CH_3), 1.02 (d, J = 7.0 Hz, 3 H, 10-CH_3), 1.07 (d, J = 7.1 Hz, 3 H, 4-CH_3), 1.22 (d, J = 6.7 Hz, 3 H, 8-CH_3), 1.30 (d, J = 6.8 Hz, 3 H, 2-CH_3), 1.31 (s, 3 H, 6-CH_3), 1.44 (dd, J_{AB} = 14.7 Hz, $J_{A7,8}$ = 10.5 Hz, 1 H, 7-H), 1.44-1.58 (m, 1 H, 13-CH_2), 1.68-1.82 (m, 2 H, 12-H, 13-CH_2CH$_3$), 1.90 (dd, J_{AB} = 14.7 Hz, $J_{B7,8}$ = 4.8 Hz, 1 H, 7-H), 1.99 (mc, 1 H, 4-H), 2.67 (s, 1 H, OH), 2.72-2.86 (m, 3 H, 2-H, 8-H, 10-H), 3.07 (s, 1 H, OH), 3.68 (mc, 1 H, 11-H), 3.72 (s, 2 H, OH), 3.88 (d, J = 9.5 Hz, 1 H, 3-H), 3.92 (s, 1 H, 3-H), 5.22 (dq, J = 9.5, 3.8 Hz, 1 H, 13-H); ^{13}C NMR ($CDCl_3$) δ 6.14, 7.17, 9.14, 10.50, 25.52, 26.44, 36.42, 40.28, 40.92, 42.33, 43.89, 70.57, 75.83, 75.99, 79.71, 80.48, carbonyl C's cannot be found; ^1H NMR (DMSO-d_6) δ 0.80 (t, J = 7.6 Hz, 3 H, 13-CH_2CH_3), 0.85 (d, J = 7.5 Hz, 6 H, 10-CH_3, 12-CH_3), 0.88 (d, J = 7.3 Hz, 3 H, 4-CH_3), 1.04 (d, J = 6.9 Hz, 3 H, 8-CH_3), 1.09 (d, J = 7.0 Hz, 3 H, 2-CH_3), 1.18 (s, 3 H, 6-CH_3), 1.19 (mc, 1 H, 7-H), 1.36-1.71 (m, 3 H, 12-H, 13-CH_2), 1.85 (dd, J = 15, 7.0 Hz, 1 H, 7-H), 2.01 (mc, 1 H, 4-H), 2.50 (mc, 1 H, 2-H), 2.66 (mc, 1 H, 8-H), 2.84 (mc, 1 H, 10-H), 3.36-3.44 (m, 2 H, 5-H, 11-OH), 3.51 (dd, J = 10.0, 5.2 Hz, 1 H, 3-H), 3.85 (dd, J = 10.5, 4.5 Hz, 1 H, 11-H), 4.19 (s, 1 H, 6-OH), 4.48 (d, J = 5.2 Hz, 1 H, 5-OH), 4.57 (d, J = 5.8 Hz, 1 H, 3-OH), 5.34 (dq, J = 9.5, 5.0 Hz, 1 H, 13-H); ^{13}C NMR (DMSO-d_6) δ 7.60 (4-CH_3), 8.21, 9.00 (10-CH_3, 12-CH_3), 10.24 (CH_2CH_3), 15.04 (2-CH_3), 17.30 (8-CH_3), 25.42 (CH_2CH_3), 26.31 (6-CH_3), 35.71 (4-C), 37.65 (7-C), 39.81 (12-C), 40.51 (10-C), 42.00 (8-C), 43.31 (2-C), 69.49 (11-C), 73.61 (13-C), 74.13 (6-C), 77.49 (3-C), 79.85 (5-C), 174.86 (1-C), 216.28 (9-C).

X-ray Analyses. See Table III and supplementary material.

Acknowledgment. This work was generously supported by the Schering AG, Berlin-Bergkamen, the Fonds der Chemischen Industrie, and the Graduiertenkolleg "Synthese und Strukturaufklärung niedermolekularer Verbindungen". We thank Professors S. F. Martin, University of Texas at Austin, TX, and E. J. Corey, Harvard University, Cambridge, MA, for providing us generous samples of erythronolide B. Additionally, we are indebted to Winfried Muench, FU-Berlin, for performing the COSY measurements.

Supplementary Material Available: Tables of analytical data (^1H and ^{13}C NMR, IR, and MS spectra and optical rotations) of intermediates and results of the single-crystal X-ray analysis of compounds **46** and **52** including positional parameters, U values, intramolecular distances, bond angles, and torsional angles (27 pages); listing of observed and calculated structure factors (43 pages). Ordering information is given on any current masthead page.

(40) Martin, J. R.; Perun, T. J.; Girolami, R. L. *Biochemistry* **1966**, *5*, 2852.

(41) (a) Sheldrick, G. M. *SHELXS 86, Program for Crystal Structure Solution*; University of Goettingen: Goettingen, Germany, 1986. (b) *XTAL 2.2. User's Manual*; Hall, S. R., Steward, J. M., Eds.; University of Western Australia Nedlands, WA, and University of Maryland, College Park, Md, 1987. (c) Keller, E. *SCHAKAL-88, Program for Graphic Representation of Molecular and Crystallographic Models*; Albert-Ludwigs-Universitaet: Freiburg, Germany, 1988.

Synthesis of Optically Active Cyclobutanones by the Photolysis of Chromium-Alkoxycarbene Complexes in the Presence of Optically Active Ene-Carbamates

Louis S. Hegedus,* Roderick W. Bates, and Björn C. Söderberg

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. *Received July 16, 1990*

Abstract: Optically active ene-carbamates derived from (*S*)-phenylglycine were allowed to photochemically react with a variety of (alkoxy)(alkyl)chromium-carbene complexes. Cyclobutanones were formed in fair to good yield with generally excellent control of stereochemistry.

Introduction

Cyclobutanones are important intermediates in the synthesis of a wide range of natural products and other complex organic molecules.[1] They are most often made by the [2 + 2] cycloaddition reaction between ketenes and olefins,[2] a process that has been the subject of several recent studies.[3] In contrast, asymmetric induction into the ketene-olefin cycloaddition process has been little studied. With the chiral auxiliary on the ketene fragment, induction was high (80-97%) with use of optically active ketene iminium salts of symmetrical ketenes,[4] but somewhat lower (~50%) in the cycloaddition of optically active (menthyloxy)(methyl)ketene to ethyl propenyl ether.[5] Similarly, cycloaddition of dichloroketene to optically active enol ethers proceeded with diastereomeric excesses ranging from 50 to >95%.[6]

Recent research in our laboratory has centered on the ketene-like reactivity of heteroatom-stabilized (Fischer) carbenes when photolyzed with visible light[7] and the use of this process to synthesize β-lactams,[8] α-amino acid esters,[9] and cyclobutanones.[10]

(1) Bellus, D.; Ernst, B. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 797.

(2) (a) Ghosez, L.; O'Donnell, J. M. *Pericyclic Reactions, Vol. II*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1988; pp 79-140. (b) Brady, W. T. *The Chemistry of Ketenes, Allenes, and Related Compounds*; Patai, S., Ed.; Interscience Publications: New York, 1980; pp 278-308. (c) Brady, W. T. *Tetrahedron* **1981**, *37*, 2949.

(3) (a) Snider, B. B. *Chem. Rev.* **1988**, *88*, 793 and references cited therein. (b) Brady, W. T.; Gu, Y. Q. *J. Org. Chem.* **1989**, *54*, 2834 and references cited therein.

(4) Houge, C.; Frisque-Hesbain, A. M.; Mockel, A.; Ghosez, L.; Rederoq, J. P.; Germain, G.; Van Meerssche, M. *J. Am. Chem. Soc.* **1982**, *104*, 2920.

(5) Fräter, G.; Muller, U.; Günther, W. *Helv. Chim. Acta* **1986**, *69*, 1858.

(6) (a) Greene, A. E.; Charbonnier, F. *Tetrahedron Lett.* **1985**, *26*, 5525. (b) Green, A. E.; Charbonnier, F.; Luche, M. J.; Moyano, A. *J. Am. Chem. Soc.* **1987**, *109*, 4752.

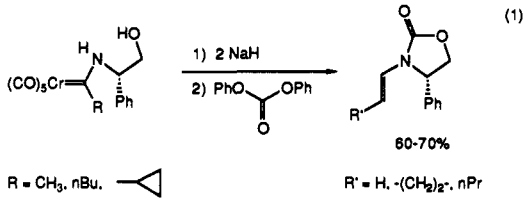
(7) Hegedus, L. S.; deWeck, G.; D'Andrea, S. *J. Am. Chem. Soc.* **1988**, 110, 2122.

(8) Hegedus, L. S.; Imwinkelried, R.; Alarid-Sargent, M.; Dvorak, D.; Satoh, Y. *J. Am. Chem. Soc.* **1990**, *112*, 1109.

(9) Hegedus, L. S.; Schwindt, M. A.; DeLombaert, S.; Imwinkelried, R. *J. Am. Chem. Soc.* **1990**, *112*, 2264.

0002-7863/91/1513-923$02.50/0

In the course of these studies, an aborted attempt to synthesize chromium–carbene complexes containing an optically active oxazolidinone chiral auxiliary instead produced optically active ene–carbamates in good yield (eq 1).[11] Since enamides had been

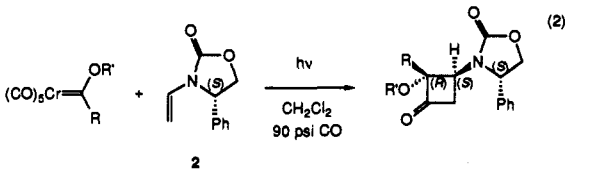


(1)

shown to be efficiently converted to amidocyclobutanones in the photoreaction with chromium–alkoxycarbene complexes,[10] this result provided an opportunity to examine asymmetric induction in this process. The results of these studies are presented in the following text.

Results and Discussion

Photolysis (Pyrex) of a variety of chromium–alkoxycarbene complexes in the presence of 2 equiv of the unsubstituted optically active (*S*)-ene–carbamate **2** under 90 psi of carbon monoxide pressure produced optically active cyclobutanones **3a–3e** in fair to good yield (eq 2). Chromium hexacarbonyl precipitated from

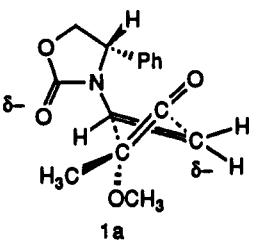


(2)

1a R = Me; R' = Me	3a 61% 94% de (+3% *SSS*)
1b R = Me; R' = Bn	3b 56% 86% de (+5% *SSS*)
1c R = Ph; R' = Me	3c 67% ≥97% de
1d R =  ; R' = Me	3d 59% ≥97% de
1e R, R' = -(CH2)4-	3e 50% ≥97% de
1f R = CH=CHCH3, R' = Me	——

solution and could be recovered in up to 90% yield by trituration with methanol, in which it is insoluble. The excess ene–carbamate could also be recovered in excellent yield. Identical yields and stereoselectivities were observed when the reaction was run in acetonitrile under 1 atm of argon, although the chromium residue could not be recovered. The major diastereoisomer of **3a–3e** was easily isolated in pure form by flash chromatography, and yields shown are for pure, single diastereoisomers.

As is usually the case with ketene–olefin cycloaddition reactions, the process was highly regio- and stereoselective.[12] In addition, it was highly diastereoselective. The stereochemical outcome of the process described in eq 2 is particularly informative since it represents a rare case that involves the cycloaddition of an unsymmetrical ketene with an optically active olefin. For this process to be stereochemically efficient, two aspects of the stereochemistry must be controlled: the absolute stereochemistry of the newly formed chiral center α to the oxazolidinone, which is determined by which face of the prochiral olefin is preferentially attacked, and the relative stereochemistry between the two newly established adjacent chiral centers, which is determined by the minimization of steric interactions between the substituents on the ketene and olefin partners in the transition state. In normal ketene–olefin cycloaddition reactions, the *more* sterically hindered cyclobutanone



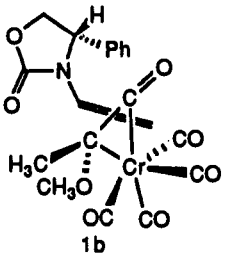
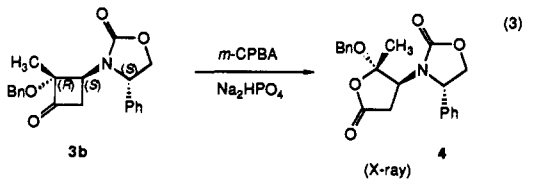


Figure 1. Proposed interaction.

predominates since it arises from the less sterically hindered transition state (see the following text). The same selectivity was observed in eq 2. The major stereoisomer had the large R group syn to the large carbamate group. Only 3–5% of the other isomer (OR syn to carbamate) was detected, and this only when the R group was methyl (**3a**, **3b**). When R was larger than methyl (**3c–3e**), the single stereoisomer shown was obtained. Thus, control of relative stereochemistry was very high. In addition, the control of absolute stereochemistry was similarly high, with the chiral carbon α to the oxazolidinone group having the *same* (*S*) absolute configuration as the chiral center in the oxazolidinone.

The absolute and relative stereochemistry of these cyclobutanones was assigned in the following manner. The major isomer of **3b** was subjected to Baeyer–Villiger oxidation (eq 3),



(3)

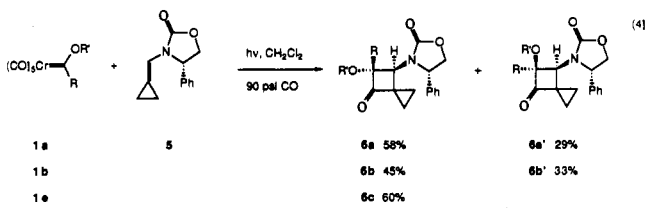
a process that proceeds with retention of the absolute stereochemistry of the migrating group,[13] and the resulting lactone was subjected to an X-ray crystallographic structure determination. This established the absolute stereochemistry as well as the relative stereochemistry of the two newly formed chiral centers to be that shown in eqs 2 and 3. The expected syn disposition of large groups in the major isomers of **3a–3c** was confirmed by ^{1}H NMR spectroscopy. For the major *SSR* isomer of **3a** and **3b**, the signal for the methyl group was upfield (δ 1.42 and 1.50) from that of the minor *SSS* isomer (δ 1.52 and 1.61) as previously observed in other cases.[14] The very minor *SRS* diastereoisomer of **3a** and **3b**, again having the two large groups syn, showed upfield shifts (δ 1.41 and 1.53) for the methyl signals.

The syn disposition of the two large groups (phenyl and oxazolidinone) in **3c** was assigned by the upfield shift of the signals for the oxazolidinone ring caused by shielding by the syn phenyl group (δ 3.52, 3.94, and 3.80 vs δ 4.90, 4.70, and 4.25 for **3a**) and the relative downfield position of the signal for the methine α to nitrogen (δ 4.90 for **3c**, δ 4.19 for **3a**). The stereochemistry of **3d** and **3e** was assigned by analogy.

The observed stereochemistry is that expected from the lowest energy "3-anti exo"[12] interaction of the ketene with the olefin, such that the larger of the two groups on the ketene (the R group) is "exo" to the less hindered prochiral face of the olefin, with the ene–carbamate in the "S-trans" conformation to minimize dipole interactions (Figure 1a). The fact that *free* ketenes are unlikely to be involved in these reactions[7-10] should not change the stereochemical bias, since the metal in any chromium–ketene complex can occupy the face opposite the olefin and thus have little effect (Figure 1b).

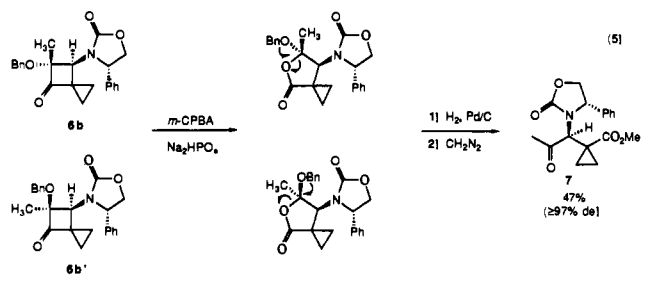
(10) Söderberg, B. C.; Hegedus, L. S.; Sierra, M. *J. Am. Chem. Soc.* **1990**, *112*, 4364.
(11) Montgomery, J.; Wieber, G. M.; Hegedus, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 6255.
(12) Valenti, E.; Pericas, M. A.; Moyano, A. *J. Org. Chem.* **1990**, *55*, 3582 and references cited therein.
(13) Mislow, K.; Brenner, J. *J. Am. Chem. Soc.* **1953**, *75*, 2318.
(14) (a) Rey, M.; Roberts, S.; Dieffenbacher, A.; Dreiding, A. S. *Helv. Chim. Acta* **1970**, *53*, 517. (b) Brady, W. T.; Roe, R., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 4618. (c) Brady, W. T.; Roe, R., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 1662. (d) See ref 10.
(15) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M. *Org. Synth.* **1987**, *65*, 140.
(16) Hafner, A.; Hegedus, L. S.; deWeck, G.; Hawkins, B.; Dötz, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 8413.

This cycloaddition reaction was not restricted to the unsubstituted ene–carbamate **2**. *gem*-Disubstituted ene–carbamate **5** also underwent this process, with reduced "syn–anti" selectivity but high asymmetric induction at the position α to nitrogen (eq 4). Stereochemical assignments were based upon the *very* close



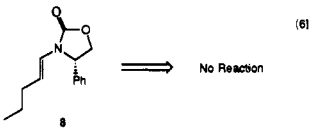
(4)

correspondence between the ^{1}H NMR spectra of **6** and **3**. Thus, for the major isomer **6a**, the signal for the methyl group syn to the nitrogen appeared at δ 1.43 vs 1.42 for **3a**, whereas for **6a'** this signal appeared at δ 1.55 vs 1.52 in the very minor *SSS* isomer of **3a**. Similarly for **6b**, the signal for the methyl group in the major isomer was at δ 1.51 vs 1.50 for **1b** and at δ 1.67 for **1b'** vs 1.61 for the *SSS* isomer of **3b**. That these differed *only* in configuration at the alkoxy-bearing position was shown by conversion of both **6b** and **6b'** to the *same* single diastereoisomer of **7** by Baeyer–Villiger oxidation/hydrogenolysis lactone cleavage (eq 5). This lack of "syn–anti" stereoselectivity is remarkable and is not easily rationalized by the conventional analysis of ketene–olefin stereochemistry presented previously. Its clarification awaits further study.



(5)

Two types of reactions failed to produce optically active cyclobutanones. α,β-Unsaturated carbene complex **1f** (R = CH=CHCH$_3$) failed to undergo the photocycloaddition to ene–carbamate **2** at all. Similarly, *trans*-ene–carbamate **8**, failed to undergo reaction, providing yet another example of the general lack of reactivity of *trans*-disubstituted olefins to cycloaddition with ketenes.[2,3,5,10]



(6)

With these limitations, the reported reaction process provides ready access to highly functionalized optically active cyclobutanones in good yield and with generally high stereoselectivity. These compounds should prove useful as intermediates in the synthesis of more complex optically active compounds.

Experimental Section

General Procedures. Melting points were taken on a Mel-Temp apparatus and are uncorrected. A Bruker IBM 200 NMR spectrometer was used for the 200-MHz ^{1}H NMR spectra, a Bruker IBM 270 NMR spectrometer for the 270-MHz ^{1}H and 67-MHz ^{13}C spectra, and a Bruker ACP 300 NMR spectrometer for the 300-MHz ^{1}H and 75-MHz ^{13}C spectra. NMR spectra were recorded in $CDCl_3$, and chemical shifts are given in δ relative to Me_4Si (δ 0, ^{1}H) or $CDCl_3$ (δ 77, ^{13}C). Assignments in the ^{13}C NMR spectra (broad band) are based on comparison of the measured substance class. IR spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrometer. Mass spectra were obtained on a V.G. Micromass Ltd. Model 16F spectrometer. Optical rotations were obtained on a Perkin-Elmer 24 polarimeter at a wavelength of 589 nm (sodium D line) by a 1.0-dm cell with a total volume of 1 mL. Specific rotation ($[\alpha]_D$) was reported in degrees per decimeter at the specified temperature and the concentration (c) given in grams per 100 mL in the specified solvent.

Flash chromatography was performed on Merck silica gel (230–400 mesh). Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

The following chemicals were prepared according to literature procedures: 3-ethenyl-6(*S*)-phenyl-2-oxazolidinone,[11] 3-(2-methylenecyclopropyl)-4(*S*)-phenyl-2-oxazolidinone,[11] 3-((*E*)-1-pentenyl)-4(*S*)-phenyl-2-oxazolidinone,[11] pentacarbonyl[(methoxy)(methyl)carbene]chromium(0),[17] pentacarbonyl[(methoxy)(cyclopropyl)carbene]chromium(0),[18] pentacarbonyl[(methoxy)((E)-1-propenyl)carbene]chromium(0),[19] and pentacarbonyl[(tetrahydropyranyl-1)-carbene]chromium(0).[20]

Dichloromethane and acetonitrile were distilled from CaH_2. Hexane was distilled at atmospheric pressure. Methanol (Fisher), ethanol (Aaper), *m*-CPBA (Aldrich, technical grade 80–90%), palladium on carbon (Lancaster), and Diazald (Aldrich) were used as received.

Cycloaddition Reactions. A solution of the carbene and the ene–carbamate in dichloromethane in a Fischer Porter pressure tube was saturated with CO (3 cycles to 90 psi of CO) and irradiated (450-W Conrad-Hanovia 7825 medium-pressure mercury lamp, Pyrex well) under 90 psi of CO overnight. The yellow-green solution was filtered through a pad of Celite, and the solvent was removed on a rotary evaporator. For compounds **3a**, **3b** and **6a**, **6a'** the crude mixture was placed in a sublimation apparatus and heated at 30–50 °C under reduced pressure (ca. 1 mmHg) until no further chromium hexacarbonyl could be obtained. The residue was preabsorbed on silica gel, applied to the top of an appropriate column, and flash chromatographed.

For other compounds, the crude mixture was triturated with methanol. The solution was removed from the precipitate of chromium hexacarbonyl by filtration through Celite, the solvent was evaporated, and the residue was dissolved in the minimum of toluene, put on top of a column of silica gel, and flash chromatographed.

Cyclobutanone 3a. Pentacarbonyl[(methoxy)(methyl)carbene]chromium(0) (475 mg, 1.9 mmol) and ene–carbamate **2** (718 mg, 3.8 mmol) in dichloromethane (20 mL) were reacted according to the general procedure. Flash chromatography (15 g of silica gel; 5%, 25%, 50% ether/hexane, ether) gave recovered ene–carbamate, two minor isomers as an inseparable mixture (31 mg, 6%), and cyclobutanone **3a** (319 mg, 61%) as a white solid: mp 133–134 °C; ^{1}H NMR (270 MHz) δ 1.42 (s, 3 H, CH_3), 2.70 (dd, 1 H, J_{vic} = 10.5, J_{gem} = 18.5 Hz, HCC=O), 3.13 (s, 3 H, OCH_3), 3.46 (dd, 1 H, J_{vic} = 9.5, J_{gem} = 18.5 Hz, HCC=O), 4.19 (dd, 1 H, J = 10.5, 9.5 Hz, CHN), 4.25 (dd, 1 H, J_{vic} = 5.5, J_{gem} = 8.5 Hz, CH_2O), 4.70 (t, 1 H, J = 8.5 Hz, CH_2O), 4.90 (dd, 1 H, J = 5.5, 8.5 Hz, PhC*H*N), 7.2–7.5 (m, 5 H, Ar); ^{13}C NMR (67 MHz) δ 206.1 (cyclobutanone C=O), 157.6 (oxazolidinone C=O), 138.5 (ipso), 129.4, 129.3, 126.6, (Ar), 96.1 (Me(MeO)*C*), 70.0, 61.8, 52.4, 48.9, 42.6 (*C*H$_2$C=O), 14.7 (C*C*H$_3$); IR (CH_2Cl_2) 1790, 1751, 1269, 1259 cm^{-1}; MS (NH_3-CI) 293 (M + NH_4^+), 276 (M + H$^+$); $[\alpha]^{26}_D$ = +73.9° (c = 1.345, CH_2Cl_2). Anal. Calcd for $C_{15}H_{17}NO_4$): C, H, N.

Minor isomers: ^{1}H NMR (200 MHz) δ 1.50 (s, 3 H, Me), 2.85 (dd, 1 H, J_{gem} = 18, J_{vic} = 10.8 Hz, HCC=O), 3.19 (s, 3 H, OMe), 3.69 (dd, 1 H, J = 9.2, 10.5 Hz, CHN), 4.0–4.4 (m, 2 H, HCC=O, CH_2O), 4.68 (t, 1 H, J = 8 Hz, CH_2O), 4.84 (dd, 1 H, J = 8, 5.4 Hz, PhC*H*N), 7.2–7.5 (m, 5 H, Ar); 1.40 (s, 3 H, Me), 2.87 (d, 2 H, J = 9.0 Hz, CH_2C=O), 3.43 (s, 3 H, OMe), 4.0–4.4 (m, 2 H, CHN and CH_2O), 4.68 (t, 1 H, J = 8.0 Hz, CH_2O), 5.17 (dd, 1 H, J = 8.0, 4.0 Hz, PhC*H*N), 7.2–7.5 (m, 5 H, Ar).

Cyclobutanone 3b. Pentacarbonyl[(benzyloxy)(methyl)carbene]chromium(0) (267 mg, 0.82 mmol) and ene–carbamate (310 mg, 1.64 mmol) in dichloromethane (18 mL) were reacted according to the general procedure. Flash chromatography (9 g of silica gel; 5%, 25%, 50% ether/hexane, ether) gave recovered ene–carbamate, two minor isomers as an inseparable mixture (26 mg, 9%), and cyclobutanone **3b** (161 mg, 56%): mp 145–147 °C; ^{1}H NMR (270 MHz) δ 1.50 (s, 3 H, CH_3), 2.79 (dd, 1 H, J_{gem} = 18.5, J_{vic} = 10.1 Hz, HCC=O), 3.69 (dd, 1 H, J_{gem} = 18.5, J_{vic} = 9.6 Hz, HCC=O), 4.15–4.30 (m, 2 H, CHN and CH_2O), 4.33 (s, 2 H, PhCH_2), 4.70 (t, 1 H, J = 8.5 Hz, CH_2O), 4.90 (dd, 1 H, J = 8.5, 6.0 Hz, PhC*H*N), 7.1–7.5 (m, 10 H, Ar); ^{13}C NMR (75 MHz) δ 206.4 (cyclobutanone C=O), 157.7 (carbamate C=O), 138.5 (ipso), 137.7 (ipso), 129.6, 129.5, 128.2, 127.7, 127.6, 126.9 (Ar), 96.2 (Me(BnO)*C*), 70.1, 67.1, 62.5, 50.2, 42.4 (*C*H$_2$C=O), 15.4 (CH_3); IR (CH_2Cl_2) 1790, 1751 cm^{-1}; MS (NH_3-Cl) 369 (M + NH_4^+), 352 (M

(17) Fischer, E. O.; Aumann, R. *Chem. Ber.* **1968**, *101*, 960.
(18) Conner, J. A.; Jones, E. M. *J. Chem. Soc., Dalton Trans* **1973**, 2119.
(19) Wulff, W. D.; Bauta, W. E.; Kaester, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642.
(20) Laltrada, L.; Licandro, E.; Maiorana, S.; Papagri, A. *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluver Academic: Dordrecht, The Netherlands, 1989; pp 149–151.

+ H$^+$); $[\alpha]^{26}_D$ = +93.2° (c = 1.61, CH_2Cl_2). Anal. Calcd for $C_{21}H_{21}NO_4$: C, H, N.

Minor isomers: ^{1}H NMR (200 MHz) δ 1.53 (s, 3 H, Me), 2.90 (d, 2 H, J = 8.5 Hz, C=OCH_2), 4.0 (dd, 1 H, J = 8.5, 4.5 Hz, CHHO), 4.4 (m, 2 H, CHHO and CHN), 4.65 (s, 2 H, PhCH_2), 5.04 (dd, 1 H, J = 5.0, 8.5 Hz, PhCHN), 7.1–7.5 (m, 10 H, Ar); 1.61 (s, 3 H, CH_3), 2.90 (m, 2 H, C=OCH_2), 4.22 (dd, 1 H, J = 8.1, 5.7 Hz, CHHO), 4.65 (s, 2 H, PhCH_2), 4.83 (dd, 1 H, J = 8.1, 5.7 Hz, PhCHN), 7.1–7.5 (m, 10 H, Ar).

Cyclobutanone 3c. Pentacarbonyl[(methoxy)(phenyl)carbene]chromium(0) (167 mg, 0.53 mmol) and ene–carbamate **2** (202 mg, 1.07 mmol) were treated according to the general procedures, except that the pressure tube was filled with glass beads. Flash chromatography (6 g of silica gel; 25%, 50% ether/hexane) gave recovered ene–carbamate and cyclobutanone **3c** (120 mg, 67%): mp 130–133 °C; ^{1}H NMR (270 MHz) δ 2.65 (dd, 1 H, J_{vic} = 9.5, J_{gem} = 19 Hz, HCC=O), 2.86 (dd, 1 H, J_{gem} = 19.0, J_{vic} = 10.0 Hz, HCC=O), 3.31 (s, 3 H, OMe), 3.52 (dd, 1 H, J = 9.0, 3.6 Hz, CH_2O), 3.80 (dd, 1 H, J = 9.0, 3.6 Hz, CH_2O), 3.94 (t, 1 H, J = 9.0 Hz, PhCHN), 4.90 (t, 1 H, J = 10.0 Hz, CHN), 7.0–7.6 (m, 10 H, Ar); ^{13}C NMR (67 MHz) δ 205.9 (cyclobutanone C=O), 158.3 (carbamate C=O), 140.1 (ipso), 133.5 (ipso), 129.7, 129.5, 129.2, 129.0, 128.7, 127.9, 125.7 (Ar), 100.8 (Ph(MeO)C), 70.5, 57.9, 53.9, 51.3, 45.1 (CH_2C=O); IR (CH_2Cl_2) 1786, 1753 cm^{-1}; MS (NH_3-Cl) 355 (M + NH_4^+), 338 (M + H$^+$); $[\alpha]^{23}_D$ = +151.8° (c = 1.78, CH_2Cl_2). Anal. Calcd for $C_{20}H_{19}NO_4$: C, H, N.

Cyclobutanone 3d. Pentacarbonyl[(methoxy)(cyclopropyl)carbene]chromium(0) (91 mg, 0.33 mmol) and ene–carbamate **2** (124 mg, 0.66 mmol) were treated according to the general procedure. Flash chromatography (6 g of silica gel; 20%, 50%, ether/hexane, ether) gave recovered ene–carbamate and cyclobutanone **3d** (59 mg, 59%): mp 122–124 °C; ^{1}H NMR (270 MHz) δ 0.40 (m, 1 H, cyclopropyl), 0.7 (m, 2 H, cyclopropyl), 1.22 (m, 1 H, cyclopropyl), 2.59 (dd, 1 H, J_{gem} = 18.0, J_{vic} = 9.9 Hz, HCC=O), 2.95 (dd, 1 H, J_{gem} = 18.0, J_{vic} = 9.9 Hz, HCC=O), 3.39 (s, 3 H, OMe), 4.21 (dd, 1 H, J = 8.5, 4.1 Hz, CH_2O), 4.58 (dd, 1 H, J = 9.9 Hz, CHN), 4.70 (t, 1 H, J = 8.5 Hz, CH_2O), 5.12 (dd, 1 H, J = 8.5, 4.1 Hz, PhCHN), 7.2–7.5 (m, 5 H, Ar); ^{13}C NMR (67 MHz) δ 204.5 (cyclobutanone C=O), 157.9 (carbamate C=O), 139.7 (ipso), 129.5, 129.1, 125.9 (Ar), 99.3 (CH(MeO)C), 70.3, 60.3, 52.6, 49.5, 44.3 (CH_2C=O), 9.2, 2.4, 1.4 (3 × cyclopropyl); IR (CH_2Cl_2) 1792, 1752 cm^{-1}; MS (NH_3-Cl) 319 (M + NH_4^+), 302 (M + H$^+$); $[\alpha]^{23}_D$ = +46.9° (c = 1.53, CH_2Cl_2). Anal. Calcd for $C_{17}H_{19}NO_4$: C, H, N.

Cyclobutanone 3e. Pentacarbonyl[(tetrahydropyranyl-1)-carbene]chromium(0) (245 mg, 0.89 mmol) and ene–carbamate **2** (336 mg, 1.78 mmol) were reacted according to the general procedure. Flash chromatography (8 g of silica gel; 25%, 50% ether/hexane, ether) gave recovered ene–carbamate and cyclobutanone **3e** (133 mg, 50%) as a white solid: mp 124–126 °C; ^{1}H NMR (200 MHz) δ 1.3–1.8 (m, 5 H, CH_2), 2.00 (m, 1 H, CH), 2.76 (dd, 1 H, J_{vic} = 10.0, J_{gem} = 18.0 Hz, HCC=O), 3.51 (dd, 1 H, J_{vic} = 8.0, J_{gem} = 18.0 Hz, HCC=O), 3.64 (brd, 1 H, J = 12.0 Hz, OC$H_2$$CH_2$), 3.9–4.0 (m, 2 H, CHN and OC$H_2$$CH_2$), 4.25 (dd, 1 H, J = 8.0, 4.3 Hz, CHHO), 4.69 (t, J = 8.0 Hz, CH_2O), 4.86 (dd, 1 H, J = 8.0, 4.3 Hz, PhCHN), 7.2–7.5 (m, 5 H, Ar); ^{13}C NMR (67 MHz) δ 206.7 (cyclobutanone C=O), 157.5 (carbamate C=O), 138.8 (ipso), 129.2, 129.1, 126.7 (Ar), 94.2 (CH_2COCH_2), 69.9, 65.1, 61.6, 52.0, 42.5 (CH_2C=O), 24.8, 19.5; IR (CH_2Cl_2) 1782, 1753 cm^{-1}; MS (NH_3-Cl) 318 (M + NH_4^+), 302 (M + H$^+$); $[\alpha]^{26}_D$ = +110.4° (c = 1.975, CH_2Cl_2). Anal. Calcd for $C_{17}H_{19}NO_4$: C, H, N.

Lactone 4. m-CPBA (237 mg, 1.37 mmol) was added to a solution of cyclobutanone **3b** (321 mg, 0.91 mmol) in dichloromethane (20 mL) containing disodium hydrogen phosphate (490 mg, 1.83 mmol). The mixture was stirred for 4 h. 2-Pentene (500 μL) was added, and the mixture was stirred for a further 0.5 h to destroy excess m-CPBA. The mixture was diluted with saturated aqueous sodium bicarbonate and extracted with dichloromethane. The organic layer was dried ($MgSO_4$) and evaporated to give the lactone **4** as a white foam: mp 108–111 °C; ^{1}H NMR (270 MHz) δ 1.64 (s, 3 H, Me), 2.25 (dd, 1 H, J_{gem} = 18.0, J_{vic} = 1.0 Hz, HCC=O), 2.89 (dd, 1 H, J_{gem} = 18.0, J_{vic} = 8.5 Hz, HCC=O), 4.24 (dd, 1 H, J = 7.0, 3.0 Hz, C=OCH), 4.41 (dd, 1 H, J = 8.5, 1.0 Hz, CHN), 4.55–4.70 (m, 2 H, CH_2O and PhCHN), 4.70 (s, 2 H, OCH_2Ph), 7.1–7.5 (m, 10 H, Ar); ^{13}C NMR δ 173.8 (OC=O), 158.0 (carbamate C=O), 139.0 (ipso), 137.1 (ipso), 129.6 (2C), 128.5, 127.9, 127.6, 126.9 (Ar), 110.6 (CH_3(BnO)C), 70.8, 65.2, 59.8, 58.7, 32.1 (CH_2C=O), 17.2 (CH_3); IR (CH_2Cl_2) 1788, 1752 cm^{-1}; MS (NH_3-Cl) 385 (M + NH_4^+), 368 (M + H$^+$); $[\alpha]^{23}_D$ = +69.6° (c = 1.465, CH_2Cl_2). Anal. Calcd for $C_{21}H_{21}NO_4$: C, H, N. A crystal suitable for X-ray analysis was obtained by slow evaporation of a toluene solution.[21]

(21) Full details of the structure determination will be published elsewhere.

Cyclobutanones 6a and 6a′. Pentacarbonyl[(methoxy)(methyl)carbene]chromium(0) (185 mg, 0.74 mmol) and ene–carbamate **5** were reacted according to the general procedure. Flash chromatography (7 g of silica gel; 25%, 30%, 50% ether/hexane, ether, dichloromethane) gave recovered ene–carbamate, cyclobutanone **6a′** (48 mg, 22%), and cyclobutanone **6a** (129 mg, 58%).

6a: mp 173–174 °C; ^{1}H NMR (270 MHz) δ 1.20 (m, 2 H, cyclopropyl), 1.43 (s, 3 H, Me), 1.55 (m, 2 H, cyclopropyl), 3.02 (s, 3 H, OMe), 3.87 (s, 1 H, CHN), 4.27 (dd, 1 H, J = 8.5, 6.0 Hz, CH_2O), 4.67 (t, 1 H, J = 8.5 Hz, CH_2O), 4.76 (dd, 1 H, J = 8.5, 6.0 Hz, PhCHN), 7.25–7.50 (m, 5 H, Ar); ^{13}C NMR (75 MHz) δ 211.3 (cyclobutanone C=O), 156.9 (carbamate C=O), 138.2 (ipso), 129.4 (2 C), 127.0 (Ar), 95.4 (Me(MeO)C), 70.2, 63.0, 59.9, 52.0, 38.6 (CC=O), 20.3, 15.7 (Me), 13.1; IR (CH_2Cl_2) 1775, 1755, 1264 cm^{-1}; MS (NH_3-Cl) 319 (M + NH_4^+), 302 (M + H$^+$); $[\alpha]^{26}_D$ = +47.5° (c = 1.475, CH_2Cl_2). Anal. Calcd for $C_{17}H_{19}NO_4$: C, H, N.

6a′: mp 154–156 °C; ^{1}H NMR (270 MHz) δ 0.40 (m, 1 H, cyclopropyl), 0.85 (m, 1 H, cyclopropyl), 1.25 (m, 2 H, cyclopropyl), 1.55 (s, 3 H, CH_3), 3.55 (s, 3 H, OMe), 4.22 (dd, 1 H, J = 9.0, 4.3 Hz, CH_2O), 4.35 (s, 1 H, CHN), 4.66 (t, 1 H, J = 9.0 Hz, CH_2O), 5.1 (dd, 1 H, J = 9.0, 4.3 Hz, PhCHN), 7.25–7.5 (m, 5 H, Ar); ^{13}C NMR (75 MHz) δ 213.1 (cyclobutanone C=O), 159.4 (carbamate C=O), 141.4 (ipso), 129.0, 128.7, 127.1 (Ar), 90.1 (Me(MeO)C), 71.2, 61.2, 59.0, 53.2, 36.5 (CC=O), 22.7, 19.0, 14.1; IR (CH_2Cl_2); 1775, 1749 cm^{-1}; MS (NH_3-Cl) 319 (M + NH_4^+), 302 (M + H$^+$); $[\alpha]^{26}_D$ = −64.9° (c = 1.44, CH_2Cl_2). Anal. Calcd for $C_{17}H_{19}NO_4$: C, H, N.

Cyclobutanones 6b and 6b′. Pentacarbonyl[(benzyloxy)(methyl)carbene]chromium(0) (176 mg, 0.54 mmol) and ene–carbamate **5** (232 mg, 1.08 mmol) were reacted according to the general procedure. Flash chromatography (6 g of silica gel; 25%, 50% ether/hexane, ether) gave recovered ene–carbamate, cyclobutanone **6b′** (67 mg, 33%), and cyclobutanone **6b** (92 mg, 45%).

6b: mp 175–177 °C; ^{1}H NMR (300 MHz), δ 1.25 (m, 2 H, cyclopropyl), 1.51 (s, 3 H, Me), 1.62 (m, 2 H, cyclopropyl), 3.95 (s, 1 H, CHN), 4.18 (d, 1 H, J = 11.0 Hz, CH_2Ph), 4.30 (d, 1 H, J = 11.0 Hz, CH_2Ph), 4.32 (dd, 1 H, J = 8.1, 5.3 Hz, CH_2O), 4.68 (t, 1 H, J = 8.1 Hz, CH_2O), 4.75 (dd, 1 H, J = 8.1, 5.3 Hz, PhCHN), 7.0–7.5 (m, 10 H, Ar); ^{13}C NMR (75 MHz) δ 211.3 (cyclobutanone C=O), 156.8 (carbamate C=O), 138.3, 138.0, (ipso), 129.5, 128.8, 128.1, 127.4, 127.2 (2 C, Ar), 95.5 (Me(BnO)C), 70.1, 66.5, 63.3, 60.6, 38.5, 20.4, 16.0, 14.1; IR (CH_2Cl_2) 1775, 1755 cm^{-1}; MS (NH_3-Cl) 395 (M + NH_4^+), 378 (M + H$^+$); $[\alpha]^{26}_D$ = +60.3° (c = 1.66, CH_2Cl_2). Anal. Calcd for $C_{23}H_{23}NO_4$: C, H, N.

6b′: mp 126–129 °C; ^{1}H NMR (270 MHz) δ 0.40 (m, 1 H, cyclopropyl), 0.90 (m, 1 H, cyclopropyl), 1.30 (m, 2H, cyclopropyl), 1.67 (s, 3 H, Me), 4.00 (dd, 1 H, J = 10.9, 5.5 Hz, CH_2O), 4.18 (t, 1 H, J = 10.9 Hz, CH_2O), 4.40 (s, 1 H, CHN), 4.70 (d, 1 H, J = 15.0 Hz, CH_2Ph), 4.90 (d, 1 H, J = 15.0 Hz, CH_2Ph), 4.92 (dd, 1 H, J = 10.9, 5.5 Hz, PhCHN), 7.2–7.5 (m, 10 H, Ar); ^{13}C NMR (75 MHz) δ 213.1 (cyclobutanone C=O), 159.4 (carbamate C=O), 141.6, 137.9 (ipso), 128.9, 128.6, 128.4, 127.8, 127.6, 127.0 (Ar), 89.9 (Me(BnO)C), 71.0, 67.7, 61.4, 58.9, 36.5, 22.8, 19.8, 14.2; IR (CH_2Cl_2) 1772, 1748 cm^{-1}; MS (NH_3-Cl) 395 (M + NH_4^+), 378 (M + H$^+$); $[\alpha]^{26}_D$ = −74.8° (c = 1.57, CH_2Cl_2). Anal. Calcd for $C_{23}H_{23}NO_4$: C, H, N.

Pentacarbonyl[(benzyloxy)(methyl)carbene]chromium(0) (108 mg, 0.37 mmol) and ene–carbamate **5** (142 mg, 0.66 mmol) were dissolved in acetonitrile (4 mL), and the solution was irradiated for 24 h. The solvent was removed, and the residue was dissolved in 1:1 ethyl acetate/hexane (10 mL) and oxidized in a light box (6 × 20 W Vitalite fluorescent bulbs) for 3 days. Filtration through Celite and flash chromatography as above gave recovered ene–carbamate and cyclobutanones **6b** and **6b′** (87 mg, 77% combined).

Cyclobutanone 6e. Pentacarbonyl[(tetrahydropyranyl-1)-carbene]chromium(0) (107 mg, 0.39 mmol) and ene–carbamate **5** (166 mg, 0.77 mmol) were reacted according to the general procedure. Flash chromatography (6 g of silica gel; 25%, 50% ether/hexane) gave cyclobutanone **6e** (77 mg, 60%) as a white solid: mp 168–171 °C. ^{1}H NMR (300 MHz) δ 1.0–1.9 (series of m, 9 H, CH_2), 2.32 (dt, 1 H, J_{gem} = 13.2, J_{vic} = $J_{vic'}$ = 3.9 Hz, OCH_2CH), 3.55 (br dt, 1 H, J_{gem} = 12.3, J_{vic} = 3.3 Hz, OC$H_2$$CH_2$), 3.69 (s, 1 H, CHN), 3.83 (dt, 1 H, J_{gem} = 12.3, J_{vic} = 3.1 Hz, OC$H_2$$CH_2$), 4.28 (m, 1 H, C$H_2$O), 4.65 (m, 2 H, PhCHN and CH_2O), 7.2–7.5 (m, 5 H, Ar); ^{13}C NMR (75 MHz) δ 211.9 (cyclobutanone C=O), 157.1 (carbamate C=O), 138.0 (ipso), 129.4, 129.3, 127.2 (Ar), 93.9 (CH_2OCCH_2), 70.1, 65.5, 63.3, 61.4, 38.2, 25.4 (2 C), 20.1, 19.8, 15.4; IR (CH_2Cl_2) 1770, 1756 cm^{-1}; MS (NH_3-Cl) 345 (M + NH_4^+), 328 (M + H$^+$); $[\alpha]^{23}_D$ = +76.2° (c = 1.355, CH_2Cl_2). Anal. Calcd for $C_{19}H_{21}NO_4$: C, H, N.

Keto Ester 7. m-CPBA (62 mg, 0.36 mmol) was added to a solution of ~2:1 mixture of cyclobutanones **6b** and **6b′** (75 mg, 0.2 mmol) in dichloromethane (1 mL) containing disodium hydrogen phosphate (128

mg, 0.48 mmol). The reaction was carried out as for lactone 4. The crude lactone was dissolved in methanol (2 mL). Palladium on carbon (10%) (43 mg) was added. The mixture was stirred for 44 h under hydrogen (1 atm), filtered through Celite, and evaporated. The residue was taken up in dichloromethane (6 mL) and treated with an excess of diazomethane swept on a stream of argon and generated by treatment of a solution of Diazald (63 mg) in ethanol (6 mL) with a solution of potassium hydroxide (18 mg) in water (100 μL). Flash chromatography (3 g of silica gel; 50%, 75% ether/hexane) gave the keto ester 7 as an oil (29 mg, 47%) contaminated with minor hydrogenolysis byproducts: ^{1}H NMR (270 MHz) δ 0.95 (m, 2 H, cyclopropyl), 1.3 (m, 2 H, cyclopropyl), 2.22 (s, 3 H, C(O)Me), 3.27 (s, 3 H, OMe), 3.84 (s, 1 H, CHN), 4.08 (dd, 1 H, J = 8.5, 4.5 Hz, CH_2O), 4.78 (t, 1 H, J = 8.5 Hz, CH_2O), 5.14 (dd, 1 H, J = 8.5, 4.5 Hz, PhCHN), 7.2-7.4 (m, 5 H, Ar); IR (film) 1754, 1723 cm^{-1}; MS (EI) 274 (M^+ - CH_3CO), 104 ($PhCHCH_2^+$).

Acknowledgment. Support for this research by National Science Foundation Grant CHE-870152 is gratefully acknowledged. A SERC/NATO Fellowship to R.W.B. is gratefully acknowledged.

Enantioselective Cyclopropane Syntheses Using the Chiral Carbene Complexes (S_{Fe})- and (R_{Fe})-$C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$. A Mechanistic Analysis of the Carbene Transfer Reaction

Maurice Brookhart,* Yumin Liu, Emma W. Goldman, Debra A. Timmers, and Gregory D. Williams

Contribution from the Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27599-3290. *Received June 7, 1990*

Abstract: Enantiomerically pure or enriched iron-carbene complexes of the type $C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$ have been prepared by three routes: (a) Diastereomeric acyl complexes $C_5H_5(CO)(PPh_2R^*)FeC(O)CH_3$ (R* = (*S*)-2-methylbutyl) have been prepared, separated by column chromatography, and converted by using standard techniques to (S_{Fe},S_P)- and (R_{Fe},S_P)-$C_5H_5(CO)(PPh_2R^*)Fe{=}CHCH_3^+$; (b) Enantiomerically enriched (76% ee) ($R_{C\alpha}$)-$C_5H_5(CO)_2FeCH(OCH_3)CH_3$ has been prepared from (*S*)-(-)-ethyl lactate and converted to enantiomerically enriched diastereomers $Cp(CO)(PR_3)$-$FeCH(OCH_3)CH_3$ (R = Me, Et). The individual diastereomers were then converted to enantiomerically enriched ethylidene complexes $C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$ (R = Me, Et); (c) Racemic acyl complexes $Cp(CO)(PR_3)FeC(O)CH_3$ (R = Me, Et) have been conveniently resolved via fractional crystallization of diastereomeric hydroxy carbene salt generated by using (*S*)-(+)- or (*R*)-(-)-10-camphorsulfonic acid. The enantiomerically pure acyl complexes were converted to the corresponding enantiomerically pure carbene complexes (S_{Fe})- and (R_{Fe})-$C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$ by using standard techniques. Enantioselective ethylidene transfer from these complexes to styrene, vinyl acetate, and isopropenyl acetate gave methylcyclopropanes in high optical yields. Ethylidene complexes $C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$ (R = Me, Et), $C_5H_5(CO)$-$(PPh_3)Fe{=}CHCH_3^+$, and $C_5H_5(CO)(PPh_2R^*)Fe{=}CHCH_3^+$ (R* = (*S*)-2-methylbutyl) were generated in the CD_2Cl_2 solution and studied by ^{1}H and ^{13}C NMR spectroscopy. At very low temperatures (ca. -100 °C) both anticlinal (major) and synclinal (minor) isomers could be detected. Equilibrium ratios and rates of interconversion of these isomers were determined by using variable temperature ^{1}H NMR spectroscopy. A mechanistic analysis of the transfer reaction is presented by using the stereochemical results obtained coupled with deuterium labeling and relative reactivity studies. It is concluded that the most likely mechanism for carbene transfer involves reaction of the olefin with the minor but more reactive synclinal isomer of $C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$ followed by backside attack of the developing electrophilic center at C_γ on the Fe-C_α bond. A rationale is offered for the differing diastereoselectivities of ethylidene transfer from $C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$ versus $C_5H_5(CO)_2Fe{=}CHCH_3^+$ to various olefins.

Introduction

Electrophilic iron-carbene complexes, $C_5H_5(CO)(L)Fe{=}CHR^+$ (L = CO, PR_3), react with nucleophilic alkenes to form cyclopropanes[1-7] (eq 1). Derivatives of $C_5H_5(CO)(L)Fe{=}CHR^+$ which have been used for carbene transfers include R = -H,[5a6a,b,d-f,h,j,k] $-CH_3$,[2a,b,3,5b-d,7,13,14] $-C_6H_5$,[2d,g,h] *c*-C_3H_5[2c,e]

(1) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. This reference contains a thorough analysis of the synthetic scope and limitations of carbene transfer reactions using $Cp(CO)(L)Fe{=}CHR^+$.

(2) (a) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 979. (c) Brookhart, M.; Studabaker, W. B.; Husk, G. R. *Organometallics* **1987**, *6*, 1141. (d) Brookhart, M.; Humphrey, M. B.; Kratzer, G. O.; Nelson, G. O. *J. Am. Chem. Soc.* **1980**, *102*, 7802. (e) Brookhart, M.; Studabaker, W. B.; Husk, G. R. *Organometallics* **1985**, *4*, 943. (f) Brookhart, M.; Studabaker, W. B.; Husk, G. R.; Humphrey, M. B. *Organometallics* **1988**, *8*, 132. (g) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099. (h) Broom, M. B. H. Ph.D. Dissertation, University of North Carolina, 1982.

(3) Brookhart, M.; Kegley, S. E.; Husk, G. R. *Organometallics* **1984**, *3*, 650.

(4) (a) Casey, C. P.; Miles, W. H.; Tukada, H. *J. Am. Chem. Soc.* **1985**, *107*, 2924. (b) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761. (c) Casey, C. P.; Miles, W. H. *Organometallics* **1984**, *3*, 808. (d) Casey, C. P.; Miles, W. H. *J. Organomet. Chem.* **1984**, *254*, 333.

(5) (a) Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1979**, *101*, 6478. (b) Kremer, K. A. M.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 1862. (c) Kremer, K. A. M.; Helquist, P. *J. Organomet. Chem.* **1985**, *285*, 231. (d) Kremer, K. A. M.; Kuo, G.-H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 6119. (e) Iver, R. S.; Kuo, G.-H.; Helquist, P. *J. Org. Chem.* **1985**, *50*, 5898. (f) O'Connor, E. J.; Brandt, S.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1987**, *109*, 3739. (g) Kuo, G.-H.; Helquist, P.; Kerber, R. C. *Organometallics* **1984**, *3*, 806.

0002-7863/91/1513-927$02.50/0