before it was partitioned between EtOAc (10 mL) and brine (5 mL). The layers were separated, and the organics were washed with brine (5 mL), and the combined aqueous layers were extracted with EtOAc (2 × 5 mL). The organics were dried ($MgSO_4$) and filtered, and the solvents were removed to give 0.7 mg of the deacylated amide as a slightly yellow oil that was used in the next step without further purification: oil; analytical TLC (silica gel F254), 1:1 EtOAc/hexane, R_f = 0.30; 270-MHz NMR ($CDCl_3$) δ 7.39-7.12 (5 H, m), 6.41 (1 H, ddd, J = 1.8, 3.9, 16.0 Hz), 5.63 (1 H, dd, J = 5.6, 15.4 Hz), 5.59 (1 H, d, J = 2.3 Hz), 5.46 (1 H, s), 5.34 (1 H, d, J = 5.3 Hz), 5.17 (1 H, ddd, J = 7.1, 7.7, 15.4 Hz), 5.15 (1 H, s), 5.05 (1 H, ddd, J = 4.4, 6.8, 16.0 Hz), 4.99 (1 H, s), 4.77-4.74 (1 H, m), 3.90 (1 H, d, J = 3.29 Hz), 3.29-3.19 (1 H, m), 2.92-2.73 (3 H, m), 2.61 (1 H, dd, J = 9.8, 13.3 Hz), 2.46-2.43 (1 H, m), 2.35-2.,26 (1 H, m), 2.23 (3 H, s), 2.13-1.96 (2 H, m), 1.15 (3 H, d, J = 7.1 Hz), 1.02 (3 H, d, J = 7.1 Hz), 0.81 (9 H, s), -0.03 (6 H, s).

The amide (0.7 mg) was dissolved in CH_3CN (0.1 mL) and cooled to 0 °C then 48% (aqueous) HF was added (1 μL, 24 μmol) and the reaction was stirred for 100 min at 0 °C and then partitioned between EtOAc (5 mL) and brine (5 mL). The organics were washed with brine (5 mL), the combined aqueous layers were bakc-extracted with EtOAc (2 × 5 mL), and then the organic portion was dried ($MgSO_4$) and filtered, and the solvents were evaporated. The residue was purified by ATLC (5 cm × 10 cm, 3:1 EtOAc/hexane) to give *dl*-C_{18}-desmethylcytochalasin D (**32**), 0.5 mg (ca. 70% for two steps): white crystals from acetone/hexane; mp 232-236 °C dec; analytical TLC (silica gel F254), 3:1 EtOAc/hexane, R_f = 0.41; MS exact mass calcd for $C_{29}H_{35}NO_6$ 493.2464, found 493.2472, error = 1.6 ppm; IR (neat, cm^{-1}) N H and OH 3340, C=O 1740, C=O 1690, C=O 1685; 270-MHz NMR ($CDCl_3$) δ 7.35-7.11 (5 H, m), 6.50 (1 H, dd, J = 1.8, 16.0 Hz), 5.77 (1 H, dd, J = 9.2, 15.4 Hz), 5.55 (1 H, dd, J = 2.4, 2.7 Hz), 5.51 (1 H, d, J = 0.9 Hz), 5.44 (1 H, s), 5.37 (1 H, ddd, J = 6.8, 7.4, 15.4 Hz), 5.10 (1 H, ddd, J = 2.7, 5.0, 16.0 Hz), 4.78-4.75 (1 H, m), 3.82 (1 H, dd, J = 1.5, 10.9 Hz), 3.35-3.25 (2 H, m), 2.94 (1 H, dd, J = 3.88, 13.3 Hz), 2.80 (1 H, dd, J = 10.0, 11.0 Hz), 2.80-2.73 (1 H, m), 2.56 (1 H, dd, J = 9.8, 13.3 Hz), 2.38-2.28 (2 H, m), 2.21 (3 H, s), 2.19-2.05 (3 H, m), 1.97 (1 H, s), 1.15 (3 H, d, J = 7.1 Hz), 1.11 (3 H, d, J = 6.8 Hz).

Acknowledgment. This work was supported by the National Institutes of Health (Grant No. CA-17918).

Supplementary Material Available: Table of mass spectral fragmentation patterns for **32**, CD, and ZE and details of the route to C_{16}-*epi*-zygosporin E (5 pages). Ordering information is available on any current masthead page.

Synthesis of Cyclobutanones by the Photolytic Reaction of Chromium Carbene Complexes with Olefins: Inter- and Intramolecular Reactions

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Abstract: Cyclobutanones were synthesized in good yield and with a high degree of stereo- and regioselectivity by the photolytic reaction between a variety of chromium alkoxycarbene complexes and olefins. Bicyclic cyclobutanones were synthesized in good yield and with a high degree of stereo- and regioselectivity by the photolysis of chromium alkoxycarbenes having remote double bonds in the alkoxy group.

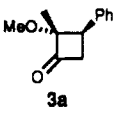
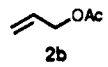
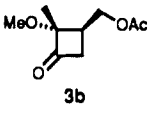
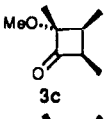
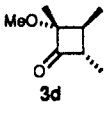
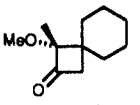
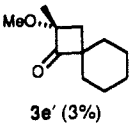
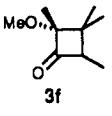
Photolysis reactions of heteroatom-stabilized (Fischer) chromium carbene complexes are becoming increasingly useful for the synthesis of novel organic compounds under exceptionally mild conditions. Thus photolysis, using visible light and a Pyrex reaction vessel, in solvents ranging from hexane through acetonitrile, of methoxycarbenes[1] and aminocarbenes[2] with imines produced β-lactams in excellent chemical yield. Use of optically active aminocarbene complexes[3] resulted in the production of optically active β-lactams in good yield and with high stereoselectivity.[4] Photolysis of aminocarbene complexes in the presence of alcohols produced α-amino acid esters.[5] During the development of these reactions it became clear that photolysis of chromium carbene complexes produced species that reacted as if they were ketenes, although no evidence for the generation of free ketenes was observed.[6] This suggested that other classes of reactions in which ketenes engaged should be examined.

Stereospecific [2 + 2] cycloaddition[7] reactions of ketenes and olefins to produce cyclobutanones[8] have been extensively developed, although the use of electron-rich O- or N-containing ketenes is uncommon.[9] In contrast, *intra*molecular versions of this process

(1) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M.; Yijun, C.; Anderson, O. P. *J. Am. Chem. Soc.* **1984**, *106*, 2680.
(2) Borel, C.; Hegedus, L. S.; Krebs, J.; Satoh, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1101.
(3) Imwinkelried, R.; Hegedus, L. S. *Organometallics* **1988**, *7*, 702.
(4) Hegedus, L. S.; Imwinkelried, R.; Alarid-Sargent, M.; Dvorak, D.; Satoh, Y. *J. Am. Chem. Soc.* **1990**, *112*, 1109.
(5) Hegedus, L. S.; Schwindt, M. A.; DeLombaert, S.; Imwinkelried, R. *J. Am. Chem. Soc.* **1990**, *112*. 2264.
(6) (a) Hegedus, L. S.; deWeck, G.; D'Andrea, S. *J. Am. Chem. Soc.* **1988**, *110*, 2122. (b) Cyclobutanones have also been produced by intramolecular trapping of chromium–vinyl ketene complexes, produced by the thermal reaction of chromium–carbene complexes with enynes, see: Wulff, W. D.; Kaisler, R. W. *Organometallics* **1985**, *4*, 1461. Korkowski, P. F.; Hoye, T. R.; Rydberg, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 2676. (c) Reaction of (phenyl)(methoxy)carbene–chromium complexes with enamides under 150 atm of CO pressure also produced cyclobutanones: Dorrer, B.; Fischer, E. O. *Chem. Ber.* **1974**, *107*, 2683. (d) Treatment of (ethoxy)(triphenylsilyl)-tungsten carbenes under 50 atm of CO produced the free ketene which was isolated and/or allowed to react with enol ethers to form cyclobutanones: Schubert, U.; Uron, J.; Hörnig, H. *J. Organomet. Chem.* **1988**, *355*, 243. Uron, J.; Schubert, U. *Ibid.* **1989**, *373*, 203.
(7) (a) Ghosez, L.; O'Donnell, J. M. *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. II, pp 79-140. (b) Brady, W. T. *Tetrahedron* **1981**, *37*, 2949. (c) Brady, W. T. *The Chemistry of Ketenes, Allenes, and Related Compounds*; Patai, S., Ed.; Interscience Publications: New York, 1980; pp 278-308.
(8) Bellus, D.; Ernst, B. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 797.
(9) (a) Reichen, W. *Chem. Rev.* **1978**, *78*, 568. (b) Brady, W. T.; Gu, Y. Q. *J. Org. Chem.* **1989**, *54*, 2834.

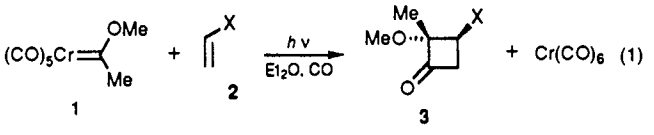
0002-7863/90/1512-4364$02.50/0

Table I. Conversion of Monoolefins to Cyclobutanones by Reaction with Complex **1**

olefin **2**	cyclobutanone **3**	yield, %[a]	isomer[b] ratio
 **2a**	 **3a**	44	10:1
 **2b**	 **3b**	31	10:1
 **2c**	 + **3d** (8%) **3c**	51	5:1
 **2d**	 + **3c** (2%) **3d**	13	5:1
 **2e**	 **3e** (45%) +  **3e'** (3%)		
 **2f**	 **3f**	77	single isomer

[a] Reported yields are for isolated, purified materials. [b] Determined by ^{1}H NMR spectroscopy, and ratio confirmed by gas chromatography. The minor isomer had the substituent syn to the methoxy group. Isomers were not separated.

have been extensively investigated, primarily by Snider[10] and Brady. The requisite ketene precursors, (alkenyloxy)acetic acids, were available from the unsaturated alcohol and bromoacetic acid, and the intramolecular cycloaddition, in general, proceeded more efficiently than did the intermolecular version. Photolysis of readily available (alkoxy)- or (alkenyloxy)carbene chromium complexes should provide ready access to these classes of electron-rich ketenes. Indeed, preliminary studies in these laboratories have shown photolysis of chromium (alkoxy)carbenes in the presence of a range of simple olefins produced cyclobutanones in excellent yield (eq 1).[11] Herein the full details of the synthesis of cyclobutanones by the inter- and intramolecular photoreactions of chromium (alkoxy)carbene complexes with olefins are reported.



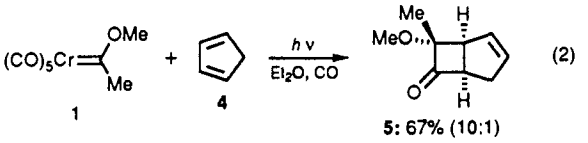
(1)

Results and Discussion

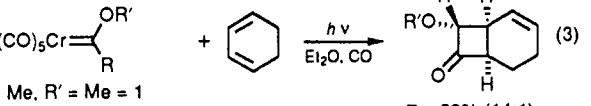
(a) Intermolecular Reactions. Because of the paucity of data concerning the use of alkoxyketenes in the synthesis of cyclobutanones, a wide range of olefinic substrates was examined for reactivity. The results of the reaction of (methoxy)(methyl)-carbene **1** with simple, unfunctionalized monoolefins are summarized in Table I.

Several features warrant comment. Although the yields of isolated, purified products were only modest, crude yields were high, and the lower isolated yields are, in part, due to the volatility of the products. The reaction was quite stereoselective, resulting in the syn disposition of large groups in the major isomer, as is usually observed in ketene–olefin cycloadditions.[7,9c,12] (The isomers could not be separated.) With *cis* and *trans*-2-butene (**2c** and **2d**), the stereochemistry of the olefin was maintained. *trans*-2-Butene was much less efficient in this reaction than was the cis isomer. In both cases, small amounts of the opposite olefin stereochemistry were observed after chromatographic purification and was attributed to epimerization of the position α to the carbonyl group. The reaction was also regioselective, giving the product resulting from attack of the more nucleophilic olefin carbon on the electrophilic ketene carbonyl carbon. (This regiochemistry was readily confirmed by the presence of a dd in the δ 2.5–3.0 region of the ^{1}H NMR spectrum due to the diastereotopic CH_2 group α to the carbonyl group.) In addition, geminally disubstituted olefin **2e** gave minor amounts of the opposite regioisomer, while **3f** gave a single stereo- and regioisomer, but the stereochemistry of the lone methyl group could not be assigned. When run in ether solvent under a modest (90 psi) pressure of carbon monoxide, the reaction was remarkably clean, and $Cr(CO)_6$, which precipitated from solution, could be recovered in 60–70% yield and reused. The expected syn stereochemistry in these products was confirmed by ^{1}H NMR spectroscopy experiments in several cases. For example, the major isomer of **3a** had the phenyl group and the methyl group syn, as evidenced by the relatively high field (δ 1.01) absorption of the methyl group due to the shielding by the syn phenyl group. The methoxy signal was at δ 3.50. In contrast the *minor* isomer had δ OMe at 3.08, indicating a syn relation to the phenyl group, and δ Me at 1.54.[13]

Cyclic conjugated dienes also underwent this reaction in good yield (eq 2 and 3). The major stereoisomer in all cases had the two large groups (R and the ring) syn and the alkoxy group exo, as evidenced by the upfield chemical shift of the R group in the major isomer relative to the minor isomer (e.g., δ 1.07 vs 1.41 for **5**; δ 1.17 vs 1.52 for **7a**; δ 1.13 vs 1.50 for **7e**; δ 1.30 vs 1.54 for **7g**).[14]



(2)



(3)

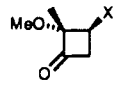
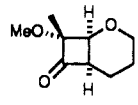
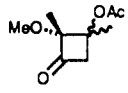
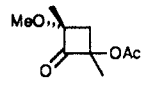
6a: R = Me, R' = Me = 1
b: R =  R' = Me
c: R = nBu, R' = Me
d: R = Ph, R' = Me
e: R = Me, R' = Et
f: R = nBu, R' = Et
g: R = Me, R' = CH_2Ph
h: R = Me, R' = TMS
i: R = PhCH=CH, R' = Me

7a: 52% (14:1)
b: 48% (20:1)
c: 46% (13:1)
d: 75% (20:1)
e: 85% (10:1)
f: 96% (14:1)
g: 70% (9:1)
h: 37% (5:1)

The reaction was not restricted to the parent carbene complex **1**, but rather tolerated a variety of alkyl and alkoxy groups (eq 3). The yields with these carbene complexes were high, and again, the same stereo- and regioselectivity as with simple cases was observed. The ease of synthesis of structurally varied alkoxycarbene complexes makes this an attractive alternative to conventional ketene methodology[7-9] for which the requisite α-alkoxy acid chlorides may be difficult to prepare. However, α,β-unsaturated carbene complexes (**6i**) failed to form cyclobutanones when photolyzed with a variety of olefins. Instead, photodecomposition of the carbene to a myriad of unidentified products occurred.

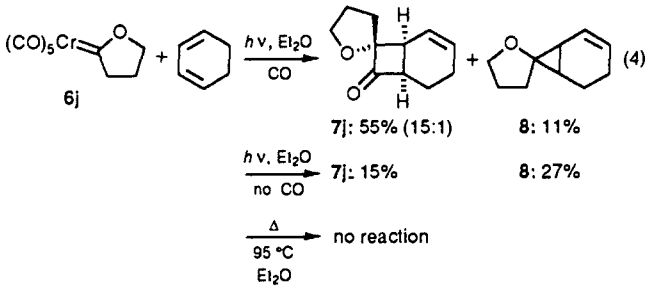
(10) Snider, B. B. *Chem. Rev.* **1988**, *88*, 793 and references cited therein.
(11) Sierra, M. A.; Hegedus, L. S. *J. Am. Chem. Soc.* **1989**, *111*, 2335.
(12) DoMinh, T.; Strausz, O. P. *J. Am. Chem. Soc.* **1970**, *92*, 1766.
(13) In related β-azetidinones, methoxy groups syn to phenyl groups appeared at ~δ 3.0, while those anti appeared at δ 3.6. See also: Bose, A. K.; Lal, B.; Manko, M. S. *Tetrahedron Lett.* **1974**, 2633.
(14) (a) Rey, M.; Roberts, S. Dieffenbacher, A.; Dreiding, A. S. *Helv. Chim. Acta* **1970**, *53*, 417. (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.

Table II. Conversion of Electron-Rich Olefins to Cyclobutanones by Reaction with Complex 1

olefin 9	cyclobutanone 10	yield, %[a]	isomer[b,c] ratio
			
9a: X = OEt	10a: X = OEt	87	6:1
9b: X = OAc	10b: X = OAc	19	20:1
9c: X = NHAc	10c: X = NHAc	96	8:1
9d: X = N 	10d: X = N 	78	7:1
 9e	 10e	80	11:1
 9f	 10f (16%)		1:1
	+  10f' (3%) single isomer		

[a] Reported yields are for isolated, purified material. [b] Determined by ^{1}H NMR spectroscopy. The minor isomer had the olefin substituent syn to the methoxy group. [c] Isomers were not separated.

The behavior of oxacyclopentylidene complex **6j** was particularly interesting (eq 4). Under the standard reaction conditions (*hν*, Et_2O, 90 psi CO) cyclobutanone **7j** was formed as the major product, along with a small amount of cyclopropane **8**. In the absence of CO, the cyclopropane was the *major* product. *Thermal* reactions of alkoxycarbene complexes with olefins normally produce cyclopropanes.[15] However heating carbene **6j** with cyclohexadiene to 95 °C in the presence and absence of CO (sealed tube) for prolonged periods resulted in no reaction at all. Instead

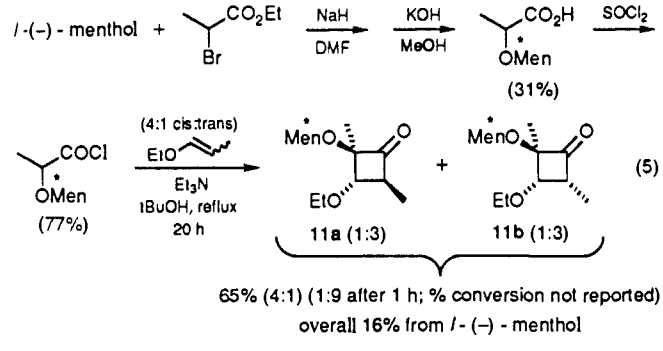


(4)

carbene **6j** was recovered in excellent yield. Since a vacant coordination site is required for cyclopropanation of electron deficient olefins, thermal, sealed-tube reactions of complex **6j** did not occur, since generation of a coordination site by CO loss was suppressed. In contrast the results shown in eq 4 imply that under photochemical conditions concentration of unsaturated complex sufficient to form cyclopropanes competitively are generated, even under modest CO pressures. Complex **6j** is unusual among alkoxycarbene complexes in that the ^{53}Cr NMR signal appears well upfield from those of noncyclic alkoxycarbenes (δ 123 vs 170–300), a fact attributed to an increase in shielding of the metal by the enforced efficient π overlap of the lone pair of electrons on oxygen with the sp^2 carbene carbon.[16] This results in an increase in stability of the carbene complex and may well make CO insertion more difficult.

Electron-rich olefins also underwent this cycloaddition reaction efficiently (Table II). Enol ethers and enamides formed cyclobutanones in excellent isolated yield and with the same stereo and regioselectivity observed with simple olefins. In contrast, enol acetates (**9b, f**) underwent reaction in only low yield, with concommitant formation of many byproducts. Allyl acetate (Table I) had similar problems. As was the case with simple olefins, gem disubstitution (**9f**) resulted in the production of two *regioisomers* (**10f, 10f'**) with the major regiosomer **10f** being a 1:1 mixture of stereoisomers and the minor regioisomer **10f'** being a single stereoisomer. In contrast to most ketene–olefin reactions large excesses of olefin were not required for good conversion, since ketene–ketene reactions are not observed in photolyses of chromium carbene complexes. Thus, with **9e** as substrate, the yield was 80% when 5 equiv of olefin is used and a respectable 65% when only 1 equiv is used. In addition, both yields and isomer distributions were insensitive to solvent and concentration. The methyl group of the major isomer again appeared upfield from that of the minor isomer (**10a**, δ 1.35 vs 1.57; **10c**, δ 1.27 vs 1.54; **10e**, δ 1.20 vs 1.56), indicative of the syn disposition of this methyl group and the heteroatom substituent from the olefinic partner in the reaction.[14c] The assigned stereochemistry was confirmed by NOE measurements on **10a** and **10c**. Thus, the irradiation of the C-2 MeO signal in **10a** resulted in strong NOE enhancement of the adjacent C-3 CH signal, whereas irradiation of the C-2 Me signal resulted in no enhancement of this same signal, indicating the syn relation of the MeO group and the C-3 CH group and confirming the assigned stereochemistry of **10a**. The same NOE measurements were carried out on **10c** with the same results.

A direct comparison of the chromium carbene route to cyclobutanones with the conventional acid chloride/tertiary amine methodology is instructive. The [2 + 2] cycloaddition of (menthyloxy)methylketene to ethyl propenyl ether was recently reported (eq 5).[17] The same reaction was carried out by using the methodology developed herein (eq 6). The processes gave similar results in many respects. The overall chemical yield of its carbene route was substantially higher, primarily because the requisite carbene **12** was synthesized in much better yield than the corresponding acid halide. The yields for the cycloaddition step were comparable, with the carbene route having a slight edge. The diastereoselectivity was identical, as was the *intrinsic* (initial) cis/trans isomer ratio about the enol ether derived fragment. (The cis enol reacts faster than the trans isomer, accounting for the preponderance of **11b**.) After 1 h, the reaction mixture in eq 5 was reported to consist of a 1:9 mixture of **11a** and **11b** (% conversion not reported). Base-catalyzed epimerization of **11b** to **11a** over the 20 h course of the reaction accounts for the final preponderance of the more stable *trans*-**11a**. In contrast, no epimerization was noted in the carbene route (eq 6) since the conditions were milder (25 °C, neutral).



(5)

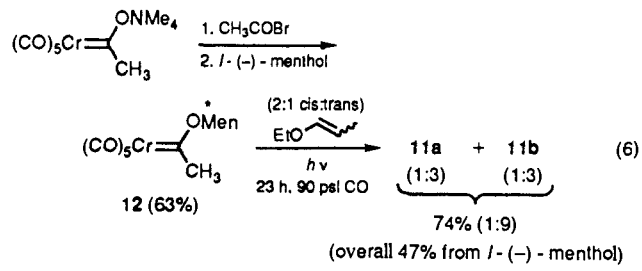
65% (4:1) (1:9 after 1 h; % conversion not reported)
overall 16% from l-(-)-menthol

A number of olefins failed to convert cleanly to cyclobutanones when irradiated with complex **1**. Acrolein dimethyl acetal, 1-chlorocyclohexene, 2-methyl-1-bromopropene, furan, 2,3-dimethyl-2-butene, phenylacetylene, diphenylacetylene, ethoxy-

(15) (a) Dötz, K. H.; Fischer, E. O. *Chem. Ber.* **1972**, *105*, 1356. (b) Wienand, A.; Reissig, H.-U. *Tetrahedron Lett.* **1988**, *29*, 2315. (c) Buckert, M.; Reissig, H.-U. *Tetrahedron Lett.* **1988**, *29*, 2319. (d) Dötz, K. H. *Angew Chem., Int. Ed. Engl.* **1984**, *23*, 587 and references therein.

(16) Hafner. A.; Hegedus, L. S.; deWeck. G.; Hawkins, B.; Dötz, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 8413.

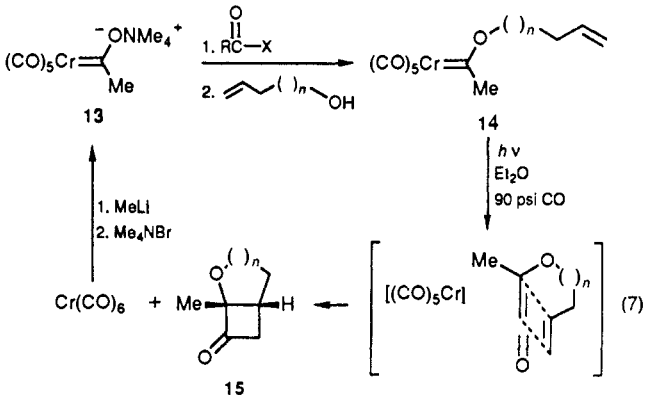
(17) Fräter, G.; Müller, U.; Günther, W. *Helv. Chem. Acta* **1986**, *69*, 1858.



acetylene, ketene diethyl acetal, ethylene, acrylonitrile, methyl acrylate, and 3-methyl-1,2-butadiene all were consumed in the reaction, but produced complex mixtures of unidentified products. However, given these limitations, the above procedure provides an efficient and convenient approach to a wide variety of alkoxycyclobutanones. The conditions are exceptionally mild and should tolerate a wide range of functional groups. The precursor carbene complexes are readily prepared and can be structurally diverse. The $Cr(CO)_6$ precursor to the carbene complexes is recovered and can be reused. This procedure should be competitive with or superior to standard methodology involving generation of alkoxyketenes by base-assisted elimination of HCl from α-alkoxy acid chlorides.[14,18]

(b) Intramolecular Reactions. The requisite (alkenyloxy)carbene complexes **14** were readily prepared by exchange of the unsaturated alcohol with (acyloxy)carbene complexes, generated by the reaction of acylate complex **13** with acetyl bromide or pivaloyl chloride (eq 7).[16] In contrast to simple alkoxycarbene complexes, those containing remote olefinic groups were relatively unstable, decomposing over the course of a few hours at room temperature and a few weeks at −20 °C. As a consequence, the ^1H NMR spectra were often broad and ill-resolved (although the ^{13}C spectra were excellent), their mass spectra, both electron impact and chemical ionization, showed only a fragment corresponding to the parent ion less $Cr(CO)_5$, and acceptable elemental analyses could not be obtained. They were best prepared and used without excessive handling.

This instability is almost certainly due to a competing, facile intramolecular cyclopropanation reaction. Indeed, phenylcarbene **16** proved to be unstable above −20 °C even under 90 psi of CO and could not be isolated, converting instead to the cyclopropane **17** in excellent yield (eq 8). *Inter*molecular cyclopropanation usually requires extended reaction times at elevated temperature and the use of activated olefins as substrates.[15] However, decomposition of carbenes related to **16** to cyclopropanes has been previously noted.[19]

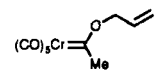
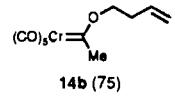
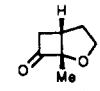
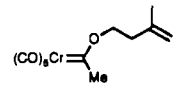
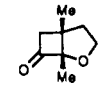
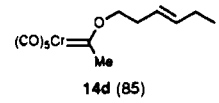
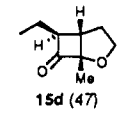
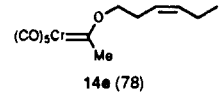
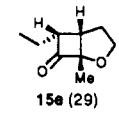
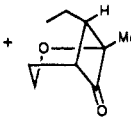
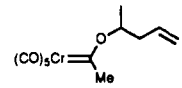
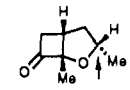
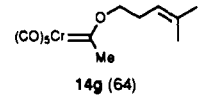
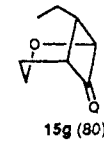
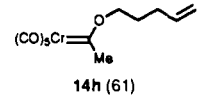
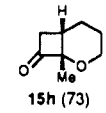
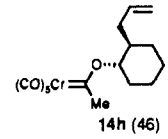
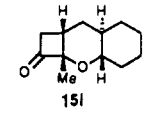
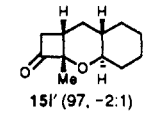
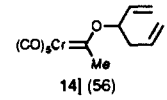
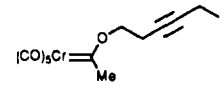
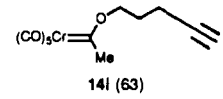
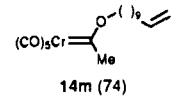
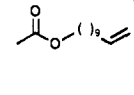


Notwithstanding this instability, most carbene complexes studied were sufficiently stable to be isolated, purified, and sub-

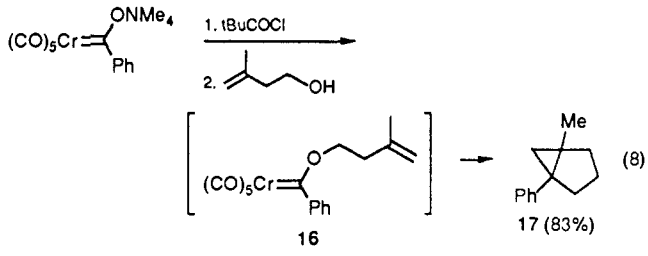
(18) (a) Aben, R. W.; Scheeren, H. W. *J. Chem. Soc., Perkin Trans. 1* **1979**, 3132. (b) Bellus, D. *J. Org. Chem.* **1979**, *44*, 1208.

(19) (a) Casey, C. P.; Shusterman, A. J. *Organometallics* **1985**, *4*, 736 and references therein. (b) Casey, C. P.; Hornung, N. L.; Kosar, W. P. *J. Am. Chem. Soc.* **1987**, *109*, 4908 and references therein (similar intramolecular cyclopropanations have been observed with tungsten carbene complexes). (c) Alvarez, C.; Parker, A.; Daran, J. C.; Rudler, H.; Rudler, M.; Unobler, C. *J. Organomet. Chem.* **1987**, *328*, 357 and references therein.

Table III. Photolytic Synthesis of Cyclobutanones from (Alkenyloxy)carbenes

alcohol	carbene complex **14** (yield, %[a])	product **15** (yield, %[b])
	 **14a** (56)	[c]
	 **14b** (75)	 **15b** (88)
	 **14c** (55)	 **15c** (62)
	 **14d** (85)	 **15d** (47)
	 **14e** (78)	 **15e** (29) +  **15e'** (22)
	 **14f** (65)	 **15f** (62, 11:1)
	 **14g** (64)	 **15g** (80)
	 **14h** (61)	 **15h** (73)
	 **14h** (46)	 **15i**  **15i'** (97, ~2:1)
	 **14j** (56)	[c]
	 **14k** (56)	[c]
	 **14l** (63)	[c]
	 **14m** (74)	 [d]
	**14n** (26)	[d]

[a] Yields (unoptimized) are of isolated, purified material. [b] Yields are of isolated purified by chromatography or distillation. [c] Complex mixture of compounds. [d] From oxidation of unconsumed carbene complex.



jected to photolytic cyclization. Photolysis (visible light through Pyrex) of these complexes in ether solvent under a modest pressure (90 psi) of carbon monoxide produced the bicyclic cyclobutanones **15** and regenerated chromium hexacarbonyl (eq 7). The results of these experiments are summarized in Table III.

These results have many features in common with those observed by using conventional acid chloride/amine ketene generation.[10] (Some differences were also noted, although these may be due to the differences in the structures of the respective ketenes—viz. CH_3 vs H.) Thus, both types of reactions failed with allyl alcohol derived ketene precursors (e.g. **14a**), which would lead to relatively unstable bicyclo[2.2.0]hexanones or bicyclo-[2.1.1]hexanones.[20] Instead a complex mixture of products was obtained. In contrast, homoallylic alcohol derived systems (e.g. **14b–g**) were generally successful with both types of reactions, although differences in the effects of olefin substitution on the two classes of reactions were substantial. With monosubstituted alkenes, the conventional route was very inefficient (~20% yield) whereas the carbene route (**14b** → **15b**) gave an excellent yield of the same type of product. Both systems gave bicyclo[3.2.0]-hexanones when the internal carbon of the alkene was more highly substituted (**14b–f**) and bicyclo[3.1.1]heptanones when the terminal carbon of the olefin was more highly substituted (**14g**), and the yields were comparable. With the carbene system, trans disubstituted ketene precursor **14d** gave bicyclo[3.2.0]hexanone **15d** in fair yield, while the cis isomer **14e** gave a mixture of bicyclo[3.2.0]hexanone **15e** and bicyclo[3.1.1]heptanone **15e′** in fair yield. In contrast, with the conventional system the cis disubstituted acid chloride did not react at all.[20] (No data was reported for the trans isomer.) (Related alkoxyketeniminium salts were more reactive, the cis compounds giving the same types of products as observed with carbene **14e**, while the corresponding trans isomer underwent acylation of the olefin rather than cyclobutanone formation.[20]) With the one carbon longer homologue (e.g. **14h**), both systems produced bicyclo[4.2.0]octanones in good yield. Carbene complex **14i** efficiently produced tricyclic products **15i** and **15i′** as an inseparable 2:1 mixture of isomers.

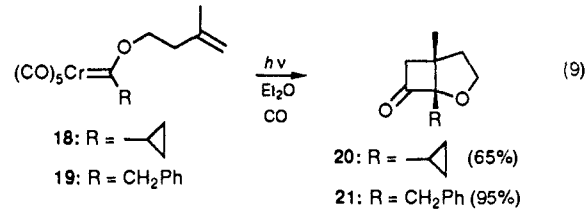
The structure assignments for **15b–i** and for **20** and **21** were based primarily on ^1H and ^{13}C NMR data, and closely parallel those described by Snider[20] for identical or closely related systems. Bicyclo[3.2.0] and -[4.2.0] systems having a CH_2 group adjacent to the cyclobutanone carbonyl group (**15b–f,h,i,j** and **20** and **21**) were characterized by a geminal coupling constant for this group of 17–19 Hz, much larger than any coupling constant found in the isomeric [3.1.1] or [4.1.1] systems, as well as a ^{13}C chemical shift for the carbonyl carbon between δ 210–217. In addition, a strong parent–ketene fragment, only possible from these ring systems, was present in the mass spectrum of each of these compounds.

In contrast, bicyclo[3.1.1] systems **15e′** and **15g** had ^{13}C chemical shift for the carbon at δ 207 and 209, respectively, and a single proton α to the carbonyl group in the ^1H NMR spectrum with J_{vic} of ~0, and 5 Hz unique to this ring system. The mass spectrum of these systems showed no fragment due to loss of ketene, since from this connectivity ketene cannot be lost.

The ^1H and ^{13}C NMR spectra of **15e′** and **15g** very closely corresponded in both chemical shift and coupling with these same systems lacking the bridgehead methyl, previously prepared by Snider.[20] There was a similar correspondence in spectra between **15d** and **15e** and the corresponding 1-desmethyl compound prepared by Snider.[20] Isomeric **15d** and **15e** were easily distinguished by the magnitude of $J_{5,6}$ = 5 Hz for *trans*-**15d** and 10.4 Hz for *cis*-**15e**.[22] Thus the structural assignments are secure.

A number of (alkenyloxy)- and (alkynyloxy)carbene complexes failed to produce cyclobutanones. In the cases of **14j–l**, the carbene was completely consumed, but a complex mixture of unidentified products was obtained. In contrast, long-chain carbene **14m** and cyclohexenylcarbene **14n** were relatively unreactive, and substantial amounts of carbene remained after 24 h of irradiation. Oxidation of the remaining carbene complex produced the esters which were isolated.

The intramolecular cycloaddition reactions of phenoxyketenes to olefins to give tricyclic cyclobutanones has also been extensively studied.[21] This chemistry is *not* accessible via related chromium carbene chemistry, since *o*-allylphenols failed to exchange with *o*-acetyl carbene complexes (as in eq 1). However, variation in the *alkyl* group on the carbene was tolerated. Both cyclopropyl complex **18** and benzyl complex **19**, efficiently converted to the corresponding cyclobutanones (eq 9).



The carbene-complex-based synthesis of bicyclic cyclobutanones complements existing methodology. The ease of preparation of a wide variety of differently substituted alkyl carbene complexes coupled with the very mild conditions for the cycloaddition process make this an attractive approach for the synthesis of functionalized or sensitive systems.

Finally, the issue of the nature of the reactive intermediates formed upon photolysis of the carbene complex remains. The following observations are germane. Photolysis of chromium carbene complexes in the presence of suitable ketene traps—olefins, alcohols, amines, imines—results in the production of the same products with the same chemo-, regio-, and stereoselectivity one would expect from the corresponding reaction of the *free* ketene were it available. However, free ketene cannot be detected in solution when these same carbene complexes are photolyzed in the absence of a ketene trap, nor are ketene-derived products, such as dimers, produced. Indeed, the (methyl)(methoxy)carbene complex **1** can be recovered in excellent yield after *days* of photolysis in the absence of a ketene trap, although photolysis in the presence of a ketene trap, results in complete consumption of the carbene complex in a matter of hours, and good yields of product are obtained. Thus, any ketene formed by photolysis must remain in close association with the chromium fragment, and must be able to revert to the original carbene complex in the absence of reactive substrates. This behavior stands in marked contrast to the behavior of less stable carbenes, which thermally and/or under a pressure of carbon monoxide liberate free ketenes which can be spectroscopically detected and in many cases, isolated [e.g. $(CO)_5Cr{=}C(Ph)_2$,[23] $(CO)_5W{=}C(OEt)(SiPh_3)$[6]].

Whatever the precise details of this process, photolysis of chromium alkoxycarbene complexes in the presence of olefins results in the efficient synthesis of cyclobutanones.

Experimental Section

General Procedure. Melting points were taken on a Mel-Temp apparatus and are uncorrected. A Bruker IBM 200 NMR spectrometer was used for the 200-MHz ^1H NMR spectra. The 270-MHz ^1H NMR and the 67-MHz ^{13}C NMR spectra were obtained on a Bruker IBM 270 NMR spectrometer. The 300-MHz ^1H NMR and the 75-MHz ^{13}C

(20) Snider, B. B.; Hui, R. A. H. F. *J. Org. Chem.* **1985**, *50*, 5167.

(21) (a) Brady, W. T.; Giang, Y. F. *J. Org. Chem.* **1985**, *50*, 5177. (b) Brady, W. T.; Marchand, A. P.; Giang, Y. F.; Wu, A.-H. *Synthesis* **1987**, 395.

(22) Rey, M.; Roberts, S. M.; Dreiding, A. S.; Roussel, A.; Vanherde, H.; Toppet, S.; Ghosez, L. *Helv. Chem. Acta* **1982**, *65*, 703.

(23) Fischer, H. *Angew Chem., Int. Ed. Engl.* **1983**, *22*, 874.

NMR spectra were obtained on a Bruker ACS-300 NMR. NMR spectra were recorded in $CDCl_3$, and chemical shifts are given in ppm relative to Me_4Si (0 ppm, ^1H), $CHCl_3$ (7.26 ppm, ^1H), or $CDCl_3$ (77 ppm, ^{13}C) unless otherwise specified. Assignments in the ^{13}C NMR spectra (broad band) are based on comparison in the measured substance class. IR spectra were recorded on a Beckmann 4240 spectrophotometer. Electron-impact (EI) and chemical-ionization (CI) 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.

For the purification of crude reaction mixtures, radial-layer (Chromatotron Model 7924) and column chromatographic techniques were applied in most cases. Merck silica gel 60 PF (for radial-layer chromatography) and Merck silica gel (230–400 mesh) or Alfa activated, neutral aluminum oxide (for column chromatography) were used as stationary phases.

Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

The following chemicals were prepared according to literature procedures: methylenecyclohexane,[24] cyclopentadiene,[25] *N*-vinylacetamide,[26] *N*-cyclohex-1-enylmorpholine,[27] ketene diethyl acetal,[28] 3-methyl-1,2-butadiene,[29] pentacarbonyl[(methoxy)(methyl)carbene]chromium(0),[30] pentacarbonyl[(cyclopropyl)(methoxy)carbene]chromium(0),[31] pentacarbonyl[(*n*-butyl)(methoxy)carbene]chromium(0),[32] pentacarbonyl[(methoxy)(phenyl)carbene]chromium(0),[30] pentacarbonyl[(methoxy)(styryl)carbene]chromium(0),[33] pentacarbonyl[(ethoxy)(methyl)carbene]chromium(0),[34] pentacarbonyl[(benzyloxy)(methyl)carbene]chromium(0),[16] pentacarbonyl(tetrahydrofuranyl-1-carbene)chromium(0),[35] pentacarbonyl[(methyl)[(tetramethylammonio)oxy]carbene]chromium(0),[36] and *trans*-2-(2-propenyl)-1-cyclohexanol.[12]

Intermolecular Reactions. Method A. To a solution of 1.0 mmol of the carbene in 20 mL of diethyl ether in a 40-mL Fischer Porter pressure tube was added 5.0 mmol of alkene with a syringe. The solution 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 colorless solution was removed by pipet from precipitated $Cr(CO)_6$ and the solvent was removed on a rotary evaporator at water aspirator pressure to give a white crystalline residue. The residue was triturated with a few milliliters of petroleum ether, and the solution was put on a 15 × 2 cm silica gel column (flash chromatography) and eluted with petroleum ether/ether to give pure cyclobutanone. Isomer ratio was determined by ^1H NMR and confirmed by GLC. In some cases the product was further purified by evaporative distillation.

Method B. The carbene (4.0 mmol) was placed in a Pyrex test tube which was sealed with a rubber septum, evacuated, and purged with argon (three times). A solution of 20.9 mmol of alkene in 40 mL of degassed acetonitrile was added with a syringe, and the resulting orange solution was irradiated overnight (450-W Conrad-Hanovia 7825 medium-pressure mercury lamp, Pyrex well). The solvent was removed on a rotary evaporator at water aspirator pressure. The yellow solid residue was dissolved in ethyl acetate, filtered through Celite, diluted with one volume of hexane, and air oxidized overnight in a light box (6 × 20 W Vitalite fluorescent bulbs). Filtration, through Celite, of the brown suspension and solvent removal on a rotary evaporator gave almost pure product. The sample was further purified, for elemental analysis, by evaporative distillation.

2-Methoxy-2-methyl-3-phenylcyclobutan-1-one (3a). From 250 mg (1.00 mmol) of pentacarbonyl[(methoxy)(methyl)carbene]chromium(0) (**1**) and 570 μL (5.00 mmol) of styrene after irradiation for 22 h and purification (petroleum ether/Et_2O, 9:1), 80 mg (0.42 mmol, 42%, 10:1 anti/syn) of **3a** as a colorless oil was obtained. *anti*-**3a**: ^1H NMR (270 MHz, $CDCl_3$) δ 7.40–7.20 (m, 5 H, Ar), 3.90 (t, 1 H, $J_{3,4} = J_{3,4'} = 10.3$ Hz, H-3), 3.50 (s, 3 H, OMe), 3.20 (dd, 1 H, $J_{4,4'} = 17.3$, $J_{4,3} = 10.3$ Hz, H-4), 2.98 (dd, 1 H, $J_{4,4'} = 17.2$, $J_{4',3} = 10.2$ Hz, H-4'), 1.01 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.01 (CO), 137.06 (ipso), 128.43, 127.58, 126.72, 95.33 (C2), 52.71 (OMe), 41.87 (C4), 38.43 (C3), 16.42 (Me); IR ($CDCl_3$) ν 1778 (CO) cm^{-1}; high-resolution mass spectrum calcd for $C_{12}H_{14}O_2$ 190.0994, $M^+ - CH_3$ 175.0759, found 175.0762.

3-(Acetoxymethyl)-2-methoxy-2-methylcyclobutan-1-one (3b). From 500 mg (2.00 mmol) of **1** and 1.08 mL (10.00 mmol) of allyl acetate in 30 mL of Et_2O after irradiation for 24 h and flash chromatography (petroleum ether/Et_2O, 6:4), 116 mg (0.62 mmol, 31%, 10:1 anti/syn) of **3b** was obtained as a colorless oil. *anti*-**3b**: ^1H NMR (300 MHz, $CDCl_3$) δ 4.33 (dd, 1 H, $J_{gem} = 11.5$, $J_{CH_{2,3}} = 6.4$ Hz, CH_2O), 4.21 (dd, 1 H, $J_{gem} = 11.6$, $J_{CH_{2,3}} = 7.5$ Hz, CH_2O), 3.34 (s, 3 H, OMe), 2.93 (dd, 1 H, $J_{4,4'} = 15.6$, $J_{4,3} = 9.8$ Hz, H-4), partly overlapping 2.88 (m, 1 H, H-3), 2.65 (dd, 1 H, $J_{4',4} = 15.6$, $J_{4',3} = 7.6$ Hz, H-4'), 2.07 (s, 3 H, Me-CO), 1.34 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.06 (CO), 170.80 (*MeCO*), 93.49 (C2), 63.60 (*CH*$_2$O), 57.21 (OMe), 43.03 (C4), 33.52 (C3), 20.81 (Me), 14.04 (Me); IR (film) ν 1783 (CO), 1741 (OCO) cm^{-1}; MS (EI) 144 ($M^+ - 42$). Anal. ($C_9H_{14}O_4$) C, H.

2-Methoxy-2,3,4-trimethylcyclobutan-2-one (3c). Through a test tube containing 300 mg (1.20 mmol) of **1** in 10 mL of MeCN was bubbled *cis*-2-butene for 10 min. The tube was sealed, irradiated for 19 h, filtered through Celite, and air oxidized for 30 h. The brown precipitate was filtered, and the solvent was removed on a rotary evaporator at water aspirator pressure to give 230 mg of a yellow oil and solid $Cr(CO)_6$. The crude mixture was evaporatively distilled to give 100 mg (0.70 mmol, 59%) of a colorless oil consisting of an inseparable mixture of 5:1:1 *anti*:*syn*-**3c**/*syn*:*syn*-**3c**/*anti*:*anti*-**3d**. *anti*:*syn*-**3c**: ^1H NMR (300 MHz, $CDCl_3$) δ 3.55 (qd, 1 H, $J_{4,3} = 11.7$, $J_{4,Me} = 7.7$ Hz, H-4), 3.29 (s, 3 H, OMe), 2.54 (qd, 1 H, $J_{3,4} = 11.7$, $J_{3,Me} = 7.5$ Hz, H-3), 1.13 (s, 3 H, Me-C2), 0.97 (d, 3 H, $J_{Me,4} = 7.7$ Hz, Me-C4), 0.91 (d, 3 H, $J_{Me,3} = 7.5$ Hz, Me-C3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.34 (CO), 94.89 (C2), 53.11 (C4), 52.73 (OMe), 34.22 (C3), 12.52 (Me), 9.72 (Me), 8.45 (Me); IR ($CHCl_3$) ν 1773 (CO) cm^{-1}; high-resolution mass spectrum calcd for $C_8H_{15}O_2$ (M^+H^+) 143.1073, found 143.1075.

2-Methoxy-2,3,4-trimethylcyclobutan-2-one (3d). From 250 mg (1.00 mmol) of **1** after irradiation for 17 h and flash chromatography (petroleum ether/Et_2O, 8:2), 22 mg (0.15 mmol, 15%) of a colorless oil consisting of an inseparable mixture of 5:1:1 *anti*:*anti*-**3d**/*syn*:*anti*-**3d**/*anti*:*syn*-**3c** was obtained. *anti*:*anti*-**3d**: ^1H NMR (300 MHz, $CDCl_3$) δ 3.32 (s, 3 H, OMe), 2.57 (qd, 1 H, $J_{4,3} = 9.6$, $J_{4,Me} = 7.0$ Hz, H-4), 2.07 (qd, 1 H, $J_{3,4} = 9.6$, $J_{3,Me} = 6.8$ Hz, H-3), 1.28 (s, 3 H, Me-C2), 1.23 (d, 3 H, $J_{Me,3} = 6.8$ Hz, Me-C3), 1.14 (d, 3 H, $J_{Me,4} = 7.1$ Hz, Me-C4); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.18 (CO), 91.68 (C2), 52.97 (OMe), 52.09 (C4), 37.32 (C3), 14.96 (Me), 13.65 (Me), 12.01 (Me); IR (film) ν 1776 (CO) cm^{-1}; MS (CI, NH_3): 160 ($M + NH_4^+$), 143 ($M + H^+$). Anal. ($C_8H_{16}O_2$) C, H.

1-Methoxy-1-methylspiro[3.5]nonan-2-one (3e). From 250 mg (1.00 mmol) of **1** and 600 μL (5.00 mmol) of methylenecyclohexane after irradiation for 21 h and flash chromatography (petroleum ether/Et_2O), 87 mg (0.48 mmol, 48%) of an inseparable 15:1 mixture of **3e** and spiro **3e'** was obtained as a colorless oil. Spiroketone **3e**: ^1H NMR (300 MHz, $CDCl_3$) δ 3.39 (s, 3 H, OMe), 2.63 (d, 1 H, $J_{3,3'} = 16.8$ Hz, H-3), 2.59 (dd, 1 H, $J_{3',3} = 16.8$, $J = 1.1$ Hz, H-3'), 1.75–1.43 (m, 7 H, CH_2), 1.32–1.17 (m, 3 H, CH_2), superimposed on 1.30 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.04 (CO), 92.46 (C1), 53.06, 51.12, 40.00, 32.83, 30.52, 25.80, 23.81, 22.77, 12.80 (Me); IR (film) ν 1778 (CO) cm^{-1}; MS (EI) 182 (M^+). Anal. ($C_{11}H_{18}O_2$) C, H.

2-Methoxy-2,3,3,4-tetramethylcyclobutan-1-one (3f). From 750 mg (3.00 mmol) of **1** and 1.67 mL (15.00 mmol) of 2-methyl-2-butene after irradiation for 31 h and flash chromatography eluting first with 20 mL of petroleum ether and then with 50 mL of petroleum ether/Et_2O (9:1), 359 mg (2.30 mmol, 71%) of almost pure **3f** as a colorless oil was obtained. The oil was evaporatively distilled to give 296 mg (1.90 mmol, 63%) of **3f**: ^1H NMR (300 MHz, $CDCl_3$) δ 3.42 (q, 1 H, $J = 7.3$ Hz, H-4), 3.33 (s, 3 H, OMe), 1.23 (s, 3 H, Me), 1.13 (s, 3 H, Me), 0.97 (d, 3 H, $J = 7.3$ Hz, Me-C4), 0.89 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.65 (CO), 94.89 (C2), 61.42 (C4), 53.90 (OMe), 38.41 (C3), 20.89 (Me), 19.32 (Me), 10.54 (Me), 7.38 (Me); IR (ilm) ν 1772 (CO) cm^{-1}; MS (EI) 156 (M^+). Anal. ($C_9H_{16}O_2$) C, H.

7-Methoxy-7-methylbicyclo[3.2.0]hept-2-en-6-one (5). From 500 mg (2.00 mmol) of **1** and 825 μL (10.00 mmol) of cyclopentadiene after irradiation for 20 h and flash chromatography (petroleum ether/Et_2O, 9:1), 205 mg (1.34 mmol, 67%, 10:1 exo/endo) of **5** was obtained as a colorless oil. *exo*-**5**: ^1H NMR (300 MHz, $CDCl_3$) δ 5.80 (qd, 1 H, $J_{3,2} = 5.8$, $J_{3,1} = J_{3,4} = J_{3,4'} = 1.9$ Hz, H-3), 5.61 (apparent qd, 1 H, $J_{2,3} =$

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5.7, $J_{2,1} = J_{2,4} = J_{2,4'} = 2.3$ Hz, H-2), 3.93 (ddd, 1 H, $J_{5,4'} = 9.5$, $J_{5,1} = 8.1$, $J_{5,4} = 1.4$ Hz, H-5), 3.33 (m, 1 H, H-1), 3.25 (s, 3 H, OMe), 2.55 (dm, 1 H, $J_{4,4'} = 17.3$ Hz, H-4), 2.35 (qdd, 1 H, $J_{4',4} = 17.3$, $J_{4',5} = 9.5$, $J_{4',3} = J_{4',2} = J_{4',1} = 2.1$ Hz, H-4'), 1.07 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.05 (CO), 134.62, 128.58, 97.34 (C7), 58.89 (C5), 52.63 (OMe), 50.84 (C1), 34.34 (C4), 12.03 (Me); IR (film) ν 1777 (CO) cm^{-1}; MS (EI) 152 (M^+). Anal. ($C_9H_{14}O_2$) C, H.

8-Methoxy-8-methylbicyclo[4.2.0]oct-2-en-1-one (7a). From 250 mg (1.00 mmol) of **1** and 470 μL (5.00 mmol) of 1,3-cyclohexadiene after irradiation for 26 h and flash chromatography (hexane/Et_2O, 95:5), 86 mg (0.52 mmol, 52%, 14:1 exo/endo) of **7a** was obtained as a pale yellow oil. *exo*-**7a**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.98 (m, 1 H, H-3), 5.83 (dd, 1 H, $J_{2,3} = 10.2$, $J_{2,1} = 4.2$ Hz, H-2), 3.79 (m, 1 H, H-6), 3.36 (s, 3 H, OMe), 2.91 (dd, 1 H, $J_{1,6} = 10.7$, $J_{1,2} = 4.3$ Hz, H-1), 2.05–1.85 (m, 3 H, H-4, H-5), 1.61 (m, 1 H, H-5'), 1.17 (s, 3 H, Me); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 210.98 (CO), 130.33, 124.71, 95.27 (C8), 53.88 (OMe), 52.60 (C6), 36.29 (C1), 21.30 (C4), 19.00 (C5), 13.03 (Me); IR (film) ν 1770 (CO) cm^{-1}; MS (EI) 166 (M^+). Anal. ($C_{10}H_{14}O_2$) C, H.

8-Cyclopropyl-8-methoxybicyclo[4.2.0]oct-2-en-7-one (7b). From 422 mg (1.53 mmol) of **6b** and 610 μL (7.64 mmol) of 1,3-cyclohexadiene after irradiation for 45 h and flash chromatography (petroleum ether/Et_2O, 95:5), 141 mg (0.73 mmol, 48%) of **7b** was isolated as a colorless oil. Only the exo isomer was observed: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (m, 2 H, H-2, H-3), 3.54 (m, 1 H, H-6), 3.35 (s, 3 H, OMe), 2.84 (dd, 1 H, $J_{1,6} = 10.6$, $J_{1,2} = 2.8$ Hz, H-1), 1.85 (m, 3 H, H-4, H-5), 1.55 (m, 1 H, H-5'), 0.82 (m, 1 H, cyclopropyl), 0.68 (m, 1 H, cyclopropyl), 0.43 (m, 2 H, cyclopropyl), 0.29 (m, 1 H, cyclopropyl); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.24 (CO), 129.56, 125.00, 97.17 (C8), 53.49, 53.18, 36.64 (C1), 21.35, 18.82, 10.10, 2.09, 1.46; IR (film) ν 1765 (CO) cm^{-1}; MS (EI) 192 (M^+). Anal. ($C_{12}H_{16}O_2$) C, H.

8-*n*-Butyl-8-methoxybicyclo[4.2.0]oct-2-en-7-one (7c). From 320 mg (1.10 mmol) of **6c** and 520 μL (5.50 mmol) of 1,3-cyclohexadiene after irradiation for 19 h and flash chromatography (petroleum ether/Et_2O, 95:5), 105 mg (0.50 mmol, 46%, 13:1 exo/endo) of **7c** was obtained as a colorless oil. *exo*-**7c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91 (td, 1 H, $J_{3,2} = 10.5$, $J_{3,4} = J_{3,4'} = 3.4$ Hz, H-3), 5.82 (dd, 1 H, $J_{2,3} = 10.3$, $J_{2,1} = 4.3$ Hz, H-2), 3.71 (ddd, 1 H, $J_{6,1} = 10.6$, $J_{6,5} = 6.3$, $J_{6,5'} = 4.3$ Hz, H-6), 3.27 (s, 3 H, OMe), 2.83 (dd, 1 H, $J_{1,6} = 10.6$, $J_{1,2} = 4.0$ Hz, H-1), 1.98–1.84 (m, 3 H), 1.77–1.19 (m, 10 H), 0.87 (t, 3 H, $J = 7.0$ Hz, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.60 (CO), 130.68, 124.50, 97.68 (C8), 53.67, 52.61, 36.18 (C1), 25.75, 24.76, 22.93, 21.30, 18.96, 13.88; IR (film) ν 1775 (CO) cm^{-1}; MS (EI) 208 (M^+). Anal. ($C_{13}H_{20}O_2$) C, H.

8-Methoxy-8-phenylbicyclo[4.2.0]oct-2-en-7-one (7d). From 203 mg (0.65 mmol) of **6d** and 305 μL (3.25 mmol) of 1,3-cyclohexadiene after irradiation for 42 h and flash chromatography (petroleum ether/Et_2O, 95:5), 111 mg (0.49 mmol, 75%) of **7d** was obtained as colorless crystals. Only *exo*-**7d** was isolated: mp 52–54 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (m, 5 H, ArH), 5.96 (m, 1 H, H-3), 5.25 (m, 1 H, H-2), 4.02 (ddd, 1 H, $J_{6,1} = 9.7$, $J_{6,5} = 6.3$, $J_{6,5'} = 3.4$ Hz, H-6), 3.17 (s, 3 H, OMe), 3.09 (m, 1 H, H-1), 2.10–1.93 (m, 3 H, H-4, H-5), 1.58 (m, 1 H, H-5'); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.40 (CO), 134.29 (ipso), 130.14, 128.05, 128.01, 127.48, 124.85, 97.90 (C8), 54.56, 54.30, 39.33 (C1), 21.11, 18.60; IR (film) ν 1775 (CO) cm^{-1}; MS (EI) 228 (M^+). Anal. ($C_{15}H_{16}O_2$) C, H.

8-Ethoxy-8-methylbicyclo[4.2.0]oct-2-en-7-one (7e). From 264 mg (1.00 mmol) of **6e** and 470 μL (5.00 mmol) of 1,3-cyclohexadiene after irradiation for 22 h and flash chromatography (petroleum ether/Et_2O, 9:1), 138 mg (0.77 mmol, 77%) of *exo*-**7e** followed by 14 mg (0.08 mmol, 8%) of *endo*-**7e** was obtained as colorless oils. *exo*-**7e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87 (td, 1 H, J = ca. 10, $J_{2,3}$ = ca. 4 Hz, H-3), 5.74 (ddd, 1 H, $J_{2,3} = 10.2$, $J_{2,1} = 4.3$, $J_{2,4}$ = ca. 2 Hz, H-2), 3.71 (ddd, 1 H, $J_{6,1} = 10.7$, $J_{6,5} = 6.2$, $J_{6,5'} = 4.5$ Hz, H-6), 3.46 (12 line, 2 overlapping qd, 2 H, $J_{gem} = 9.0$, $J = 7.0$ Hz, OCH_2), 2.80 (ddd, 1 H, $J_{1,6} = 10.6$, $J_{1,2} = 4.3$, $J_{1,4} = 1.5$ Hz, H-1), 1.93–1.80 (m, 3 H, H-4, H-5), 1.52 (m, 1 H, H-5'), 1.13 (s, 3 H, Me), 1.11 (t, 3 H, $J = 7.0$ Hz, CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.64 (CO), 130.21, 124.71, 94.78 (C8), 60.60 (OCH_2), 53.79 (C6), 36.54 (C1), 21.25, 18.92, 15.63, 13.76; IR (film) ν 1775 (CO) cm^{-1}; MS (EI) 180 (M^+). Anal. ($C_{11}H_{16}O_2$) C, H.

endo-**7e**: ^{1}H NMR (300 MHz. $CDCl_3$) δ 5.93 (m, 1 H, H-3), 5.82 (m, 1 H, H-2), 3.70 (qd, 1 H, $J_{gem} = 9.0$, $J = 7.0$ Hz, OCH_2), 3.54 (qd, 1 H, $J_{gem} = 9.0$, $J = 7.0$ Hz, OCH_2), 3.40 (ddd, 1 H, $J_{6,1} = 9.3$, $J_{6,5} = 6.0$, $J_{6,5'} = 3.0$ Hz, H-6), 2.76 (m, 1 H, H-1), 2.11–1.92 (m, 3 H, H-4, H-5), 1.59–1.50 (m, 1 H, H-5'), 1.50 (s, 3 H, Me), 1.15 (t, 3 H, $J = 7.1$ Hz, CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.90 (CO), 129.83, 123.91, 91.15 (C8), 60.91 (OCH_2), 49.47 (C6), 37.43 (C1), 21.10, 21.01, 18.10, 15.74; IR (film) ν 1770 (CO) cm^{-1}; MS (EI) 180 (M^+). Anal. ($C_{11}H_{16}O_2$) C, H.

8-*n*-Butyl-8-ethoxybicyclo[4.2.0]oct-2-en-7-one (7f). From 292 mg (0.95 mmol) of **6f** and 470 μL (5.00 mmol) of 1,3-cyclohexadiene after irradiation for 24 h and flash chromatography (petroleum ether/Et_2O, 95:5), 203 mg (0.91 mmol, 96%, 14:1 exo/endo) of **7f** as a colorless oil. *exo*-**7f**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (td, 1 H, $J_{3,2} = 10.3$, $J_{3,4} = 4.0$ Hz, H-3), 5.85 (dd, 1 H, $J_{2,3} = 10.4$, $J_{2,1} = 4.3$ Hz, H-2), 3.77 (ddd, 1 H, $J_{6,1} = 10.6$, $J_{6,5} = 6.5$, $J_{6,5'} = 4.1$ Hz, H-6), 3.48 (12 line m, 2 H, $J = 7.1$ Hz, OCH_2), 2.87 (m, 1 H, H-1), 1.95 (m, 2 H), 1.79–1.22 (m, 8 H), 1.19 (t, 3 H, $J = 7.0$ Hz, OCH_2CH_3), 0.90 (t, 3 H, $J = 7.0$ Hz, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.75 (CO), 130.52, 124.54, 97.31 (C8), 60.32 (OCH_2), 53.59 (C6), 36.44 (C1), 26.30, 24.85, 22.89, 21.26, 18.88, 15.51, 13.84; IR (film) ν 1770 (CO) cm^{-1}) MS (EI) 222 (M^+). Anal. ($C_{14}H_{22}O_2$) C, H.

8-(Benzyloxy)-8-methylbicyclo[4.2.0]oct-2-en-7-one (7g). From 326 mg (1.00 mmol) of **6g** and 470 μL (5.00 mmol) of 1,3-cyclohexadiene after irradiation for 23 h and flash chromatography (hexane/Et_2O, 9:1), 153 mg (0.63 mmol, 63%) of *exo*-**7g** followed by 16 mg (0.07 mmol, 7%) of *endo*-**7g** was obtained as colorless oils. *exo*-**7g**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.29 (m, 5 H, ArH), 5.96 (td, 1 H, $J_{3,2} = 10.3$, $J_{3,4} = 3.8$ Hz, H-3), 5.82 (ddd, 1 H, $J_{2,3} = 10.4$, $J_{2,1} = 4.4$, $J_{2,4} = 2.2$ Hz, H-2), 4.58 (d, 1 H, $J_{gem} = 11.1$ Hz, $ArCH_2$), 4.52 (d, 1 H, $J_{gem} = 11.1$ Hz, $ArCH_2$), 3.84 (ddd, 1 H, $J_{6,1} = 10.7$, $J_{6,5} = 6.4$, $J_{6,5'} = 4.2$ Hz, H-6), 2.96 (ddd, 1 H, $J_{1,6} = 10.7$, $J_{1,2} = 3.9$, $J = 1.5$ Hz, H-1), 1.96 (m, 3 H, H-4, H-5), 1.58 (m, 1 H, H-5'), 1.30 (s, 3 H, Me); ^{13}C NMR (67 MHz, $CDCl_3$) δ 210.89 (CO), 138.22 (ipso), 130.46, 128.28, 127.51, 124.68, 95.35 (C8), 67.59 (OCH_2), 54.14 (C6), 36.84 (C1), 21.34, 19.00, 13.90; IR (film) ν 1770 (CO) cm^{-1}; MS (EI) 242 (M^+). Anal. ($C_{16}H_{18}O_2$) C, H.

endo-**7g**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.40–7.25 (m, 5 H, ArH), 5.96 (m, 2 H, H-2, H-3), 4.80 (d, 1 H, J = 11.0 Hz, $ArCH_2$), 4.67 (d, 1 H, J = 11.1 Hz, $ArCH_2$), 3.47 (m, 1 H, H-6), 2.88 (dd, 1 H, $J_{1,6} = 9.6$, $J_{1,2} = 3.4$ Hz, H-1), 2.05 (m, 4 H, H-4, H-5), 1.54 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.96 (CO), 138.64 (ipso), 131.54, 128.20, 127.25, 124.11, 91.19 (C8), 67.62 (OCH_2), 49.69 (C6), 37.65 (C1), 21.36, 21.17, 18.14; IR (film) ν 1765 (CO) cm^{-1}; MS (EI) 242 (M^+). Anal. ($C_{16}H_{18}O_2$): C, H.

8-Methyl-8-[(trimethylsilyl)oxy]bicyclo[4.2.0]oct-2-en-7-one (7h). To 618 mg (2.00 mmol) of pentacarbonyl[(methyl)[(tetramethylammonio)oxy]carbene]chromium(0) in 30 mL of Et_2O, under argon atmosphere at −20 °C was added with a syringe 280 μL (2.20 mmol) of chlorotrimethylsilane. The reaction mixture was stirred for 1 h at −20 °C, saturated with CO (3 cycles to 90 psi), and irradiated at ambient temperature for 17 h at 90 psi of CO. The precipitate formed was removed by filtration through Celite, the Celite was washed with 30 mL of Et_2O, and the solvent was removed on a rotary evaporator at water aspirator pressure. The crystalline residue was triturated with ca. 3 × 1 mL of petroleum ether and filtered through a disposable pipet filled with 3 cm of silica gel, and the silica was washed with petroleum ether (20 mL). The solvent was removed (rotary evaporator) to give an oil that was immediately flash chromatographed (16 × 2 cm column, petroleum ether/Et_2O, 95:5) to give 164 mg (0.73 mmol, 37%, 5:1 exo/endo) of **7h** as a colorless oil. *exo*-**7h**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85 (m, 2 H, H-2, H-3), 3.78 (ddd, 1 H, $J_{6,1} = 10.9$, $J_{6,5} = 6.3$, $J_{6,5'} = 5.5$ Hz, H-6), 2.67 (ddd, 1 H, $J_{1,6} = 10.9$, $J_{1,2} = 3.8$, $J = 1.9$ Hz, H-1), 1.94–1.78 (m, 3 H, H-4, H-5'), 1.59 (qd, 1 H, $J_{5,5'} = 13.5$ Hz, $J_{5,4} = J_{5,4'} = J_{5,6} = 6.8$ Hz, H-5), 1.18 (s, 3 H, Me), 0.11 (s, 9 H, $SiMe_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.60 (CO), 129.99, 124.73, 91.96 (C8), 54.61 (C6), 39.18 (C1), 21.44, 19.13, 18.85, 1.46 (3C, $SiMe_3$); IR (film) ν 1779 (CO) cm^{-1}; MS (EI) 224 (M^+). Anal. ($C_{12}H_{20}O_2Si$) C, H.

Spiro[bicyclo[4.2.0]oct-2-ene-8,1'-2'-oxacyclopentane]-7-one (7j) and Spiro[bicyclo[4.1.0]hept-2-ene-7,1'-2'-oxacyclopentane] (8). From 262 mg (1.00 mmol) of **6j** and 470 μL (5.00 mmol) of 1,3-cyclohexadiene after irradiation for 50 h and flash chromatography (petroleum ether/Et_2O, 9:1), 17 mg (0.11 mmol, 11%) of **8** followed by 97 mg (0.55 mmol, 55%, 15:1 exo/endo) of **7j** was obtained as colorless oils. *exo*-**7j**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.94 (11 line m, 1 H, $J_{3,2} = 10.1$, $J_{3,4} = 5.7$, $J_{3,4'} = 4.2$, $J_{3,1} = 1.8$ Hz, H-3), 5.80 (tdd, 1 H, $J_{2,3} = 10.1$, $J_{2,1} = 4.1$, $J_{2,4} = J_{2,4'} = 2.0$ Hz, H-2), 3.95–3.79 (m, 2 H, H-3'), 3.45 (td, 1 H, $J_{6,1} = 10.4$, $J_{6,5} = J_{6,5'} = 7.1$ Hz, H-6), 2.88 (10 line m, 1 H, $J_{1,6} = 10.4$, $J_{1,2} = 4.2$, $J_{1,4} = J_{1,4'} = 1.7$ Hz, H-1), 2.00–1.76 (m, 6 H), 1.69 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.37 (CO), 130.23, 124.06, 99.33 (C8), 69.26 (C3'), 52.55 (C6), 36.83 (C1), 28.44, 25.76, 21.52, 19.20; IR (film) ν 1778 (CO) cm^{-1}; MS (EI) 178 (M^+). Anal. ($C_{11}H_{14}O_2$) C, H.

8: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86 (m, 1 H, H-3), 5.68 (m, 1 H, H-2), 3.85 (m, 1 H, H-3'), 3.67 (m, 1 H, H-3'), 2.03–1.76 (m, 7 H), 1.58 (m, 1 H), 1.26 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 125.66, 122.02, 73.22 (C7), 68.53 (C3'), 33.61, 24.92, 22.72, 21.51, 21.38, 16.12; IR (film) ν 3028, 2923, 2862, 1642, 1456, 1137, 1066, 1026, 1003, 929, 716 cm^{-1}; MS (EI) 150 (M^+). Anal. ($C_{10}H_{14}O$) C, H.

Similar amounts and procedures as described above but without CO atmosphere irradiated for 122 h gave after chromatography 41 mg (0.27 mmol, 27%) of **8** followed by 27 mg (0.15 mmol, 15%) of **7j**.

3-Ethoxy-2-methoxy-2-methylcyclobutan-1-one (10a). From 1.00 g (4.00 mmol) of **1** and 2.00 mL (20.9 mmol) of ethyl vinyl ether in 40 mL of degassed MeCN (method B) after irradiation for 14 h followed by air oxidation for 18 h and after filtration through Celite, 550 mg (3.78 mmol, 87%, 6:1 anti/syn) of **10a** was obtained as a pale yellow oil. *anti*-**10a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.18 (dd, 1 H, $J_{3,4}$ = 8.1, $J_{3,4'}$ = 7.6 Hz, H-3), 3.55 (q, 1 H, J = 7.1 Hz, OCH_2), overlapping 3.53 (q, 1 H, J = 7.0 Hz, OCH_2), 3.35 (s, 3 H, OMe), 2.93 (dd, 1 H, $J_{4,4'}$ = 17.9, $J_{4,3}$ = 8.4 Hz, H-4), 2.79 (dd, 1 H, $J_{4',4}$ = 17.9, $J_{4',3}$ = 7.4 Hz, H-4'), 1.35 (s, 3 H, Me), 1.20 (t, 3 H, J = 7.0 Hz, CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.61 (CO), 95.08 (C2), 71.06 (C3), 65.99 (OCH_2), 52.61 (OMe), 46.62 (C4), 15.10 (Me), 13.45 (Me); IR (film) ν 1783 (CO) cm^{-1}; high-resolution mass spectrum calcd for $C_8H_{14}O_3$ 158.0943, found 158.0936.

3-Acetoxy-2-methoxy-2-methylcyclobutan-1-one (10b). From 250 mg (1.00 mmol) of **1** and 460 μL (5.00 mmol) of vinyl acetate in 20 mL of Et_2O after irradiation for 23 h and evaporative distillation, 32 mg (0.19 mmol, 19%) of **10b** was obtained as a colorless oil. A ca. 90% purity was obtained (GLC), further purification was not possible: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.33 (dd, 1 H, $J_{3,4}$ = 8.8, $J_{3,4'}$ = 7.1 Hz, H-3), 3.37 (s, 3 H, OMe), 3.19 (dd, 1 H, $J_{4,4'}$ = 18.5, $J_{4,3}$ = 8.8 Hz, H-4), 2.92 (dd, 1 H, $J_{4'4}$ = 18.5, $J_{4',3}$ = 7.1 Hz, H-4'), 2.12 (s, 3 H, MeCO), 1.35 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.90 (CO), 170.26 (MeCO), 95.07 (C2), 65.78 (C3), 52.76 (OMe), 46.94 (C4), 20.58 (*Me*CO), 14.05 (Me); IR (film) ν 1790 (CO), 1748 (OCO) cm^{-1}.

3-(*N*-Acetylamino)-2-methoxy-2-methylcyclobutan-1-one (10c). From 250 mg (1.00 mmol) of **1** and 425 mg (5.00 mmol) of *N*-vinylacetamide after irradiation for 24 h followed by flash chromatography eluting with first 40 mL of hexane and then 100 mL of Et_2O gave 341 mg (4.00 mmol) of *N*-vinylacetamide and then eluting with 200 mL of CH_2Cl_2/MeOH (8:2) gave 165 mg (0.95 mmol, 96% 8:1 anti/syn) of almost pure **10c**. The product was further purified by evaporative distillation to give 131 mg (0.77 mmol, 77%, 8:1 anti/syn) of **10c** as a colorless oil. *anti*-**10c**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.60 (d, 1 H, $J_{NH,3}$ = 6.8 Hz, NH), 4.66 (q, 1 H, J = 8.7, H-3), 3.34 (s, 3 H, OMe), 3.08 (dd, 1 H, $J_{4,4'}$ = 18.0, $J_{4,3}$ = 9.9 Hz, H-4), 2.83 (dd, 1 H, $J_{4',4}$ = 18.1, $J_{4',3}$ = 8.6 Hz, H-4'), 2.01 (s, 3 H, Me-CO), 1.27 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.09 (CO), 170.48 (NCO), 95.08 (C2), 52.60 (OMe), 45.82 (C4), 44.04 (C3), 22.96 (*Me*CO), 14.21 (Me); IR ($CHCl_3$) ν 1787 (CO), 1679 (NCO) cm^{-1}; high-resolution mass spectrum calcd for $C_8H_{13}NO_2$ 171.0896, found 171.0892.

2-Methoxy-2-methyl-3-(2-oxo-1-pyrrolidinyl)cyclobutan-1-one (10d). From 250 mg (1.00 mmol) of **1** and 565 μL (5.00 mmol) of *N*-vinyl-2-pyrrolidone after irradiation for 40 h followed by flash chromatography eluting with first 75 mL of Et_2O and then Et_2O/MeOH (9:1), 155 mg (0.78 mmol, 78%, 7:1 anti/syn) of **10d** was obtained as a colorless oil. *anti*-**10d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.33 (t, 1 H, $J_{3,4}$ = $J_{3,4'}$ = 9.8 Hz, H-3), 3.44 (dd, 1 H, $J_{4,4'}$ = 18.2, $J_{4,3}$ = 9.2 Hz, H-4), partly overlapping 3.35 (m, 2 H, NCH_2), 3.24 (s, 3 H, OMe), 2.85 (dd, 1 H, $J_{4'4}$ = 18.1, $J_{4',3}$ = 10.5 Hz, H-4'), 2.29 (apparent dt, 2 H, J_1 = 8.1, J_2 = 2.0 Hz, $COCH_2$), 1.94 (m, 2 H, CH_2), 1.16 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.01 (CO), 175.62 (NCO), 96.00 (C2), 52.18 (OMe), 47.91 (C3), 46.97 (C4), 41.75 (NCH_2), 31.16 (CH_2CO), 17.94 (CH_2), 13.75 (Me); IR ($CHCl_3$) ν 1790 (CO), 1679 (NCO) cm^{-1}; high-resolution mass spectrum calcd for $C_{10}H_{15}NO_3$ 197.1052, found 197.1049.

8-Methoxy-8-methyl-2-oxabicyclo[4.2.0]octan-7-one (10e). A test tube containing 1.00 g (4.00 mmol) of **1** and 2.0 mL (21.90 mmol) of 3,4-dihydro-2*H*-pyran in 40 mL of MeCN (method B) was irradiated for 14 h and air oxidized for 30 h. After Celite filtration and distillation 550 mg (3.21 mmol, 80%, 11:1 exo/endo) of **10e** was obtained as a colorless oil. *exo*-**10e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.96 (d, 1 H, $J_{1,6}$ = 6.5 Hz, H-1), 3.74 (m, 1 H, H-3), 3.56 (m, 1 H, H-3'), 3.22 (s, 3 H, OMe), 2.00 (m, 1 H, H-6), 1.69–1.29 (m, 4 H, H-4 and H-5), 1.20 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.84 (CO), 96.70 (C8), 70.67 (C1), 64.68 (C3), 55.04, 53.12, 21.91 (CH_2), 18.27 (CH_2), 9.15 (Me); IR ($CHCl_3$) ν 1782 (CO) cm^{-1}; high-resolution mass spectrum calcd for $C_9H_{14}O_3$ 170.0943, found 170.0948.

3-Acetoxy-2,3-dimethyl-2-methoxycyclobutan-1-one (10f). From 500 mg (2.00 mmol) of **1** and 1.30 mL (10.00 mmol) of 2-acetoxy-1-propene followed by irradiation for 15 h and flash chromatography (petroleum ether/Et_2O, 8:2), 62 mg (0.33 mmol, 16%, 1:1 syn/anti) of **10f** was obtained together with 8 mg (0.07 mmol, 3%) of **10f'** as colorless oils. The products were not separable. *anti*- and *syn*-**10f**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.51 (d, 1 H, $J_{4,4'}$ = 18 Hz, H-4), 3.47 (s. 3 H, OMe), 3.41 (s, 3 H, OMe), 3.24 (d, 1 H, $J_{4,4'}$ = 18.3 Hz, H-4), 3.01 (d, 1 H, $J_{4',4}$ = 18.2 Hz, H-4'), 3.00 (d, 1 H, $J_{4',4}$ = 17.9 Hz, H-4'), 2.10 (s, 6 H, OAc), 1.64 (s, 3 H. Me), 1.59 (s, 3 H, Me), 1.46 (s, 3 H, Me), 1.37 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.21 (CO), 205.77 (CO), 170.31 (Me-*C*O), 169.83 (Me-*C*O), 93.39 (C2), 93.34 (C2), 56.37, 53.92, 53.76. 52.91. 50.32. 38.68, 21.42, 21.37, 19.93, 18.38, 13.65, 13.15; IR (film) ν 1789 (CO), 1746 (OCO) cm^{-1}; MS (EI) 158 (M^+ – CO). Anal. ($C_9H_{14}O_4$) C, H.

(*S*,*S*,*R*)-, (*S*,*R*,*S*)-, (*S*,*S*,*S*)-, and (*S*,*R*,*R*)-2,4-Dimethyl-3-ethoxy-2-(menthyloxy)cyclobutan-1-one (11a and 11b). From 374 mg (1.00 mmol) of **12** and 550 μL (5.00 mmol) of ethyl 1-propenyl ether (2:1 cis/trans) in 20 mL of Et_2O after irradiation for 23 h and flash chromatography eluting with first petroleum ether then petroleum ether/Et_2O (9:1), 218 mg (0.74 mmol, 74%) of the title compounds was obtained as a colorless oil consisting of a 81(*S*,*S*,*R*)/9(*S*,*R*,*S*)/3(*S*,*S*,*S*)/1(*S*,*R*,*R*) mixture. Spectral data was in complete accordance with literature values.[17]

Pentacarbonyl[*l*-(–)-(menthyloxy)(methyl)carbene]chromium(0) (12). Acetyl bromide (0.40 g, 3.25 mmol) dissolved in 5 mL of CH_2Cl_2 was added by syringe to a solution of 1.00 g (3.24 mmol) of pentacarbonyl-[(methyl)[(tetramethylammonio)oxy]carbene]chromium(0) in 50 mL of CH_2Cl_2, at –40 °C (dry ice/acetone) under argon atmosphere. The resulting deep brown-red solution was stirred at –40 °C for 30 min followed by the addition of 0.50 g (3.21 mmol) of *l*-(–)-menthol dissolved in 5 mL of CH_2Cl_2. After 6 h at –40 °C, the reaction mixture was allowed to reach room temperature overnight. The solvent was removed on a rotary evaporator (water aspirator) to give a yellow solid. Hexane was added, and insoluble material was removed by filtration through Celite. The yellow solution was washed with saturated $NaHCO_3$ (aqueous) and brine and dried over $MgSO_4$(s) followed by solvent removal. The crude yellow oil was flash chromatographed, eluting with hexane to give, after solvent removal, 0.76 g (2.03 mmol, 63%) of **12** as an orange oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.03 and 4.74 (br s, 1 H, rotamers, OCH), 2.96 (br s, 3 H, Me), 2.20–1.05 (m, 9 H), 0.96 (br s, 6 H, $CHMe_2$), 0.81 (br s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 2 rotamers) δ 354.73 (Cr=C), 353.74 (Cr=C), 224.19 (*trans*-CO), 223.20 (*trans*-CO), 216.65 (*cis*-CO), 93.50 (OCH), 87.79 (OCH), 51.16 (Cr=C*Me*), 47.88 (Cr=C*Me*), 42.17, 41.78, 41.24, 41.33, 41.08, 33.87, 31.11, 26.43, 23.97, 23.07, 22.58, 21.85, 21.36, 16.12, 14.90; IR (film) ν 2045 (*trans*-CO), 1925 (*cis*-CO, br) cm^{-1}; MS (CI, NH_3) 271 (M – 4 CO + H^+), 270 (M^+ – 4 CO).

General Procedure for the Preparation of the Chromium Carbenes 14a–n, 16, 20, and 21. In an oven-dried 200-mL Airless flask equipped with a stir bar 10 mmol of pentacarbonyl[(tetramethylammonio)carbene]chromium salt was dissolved in 150 mL of methylene chloride. The solution was put under an argon atmosphere and cooled to –40 °C with an acetone/dry ice bath.[13] To the faint yellow solution was added 12.00 mmol of either pivaloyl chloride or acetyl bromide by syringe. The reaction mixture was stirred at –35 ± 5 °C for 1 h (the color changed slowly to deep red-brown) after which 12.00 mmol of alcohol dissolved in 6 mL of CH_2Cl_2 was added by syringe. The solution was stirred for 3 h at –35 °C followed by slow warming to room temperature without removing of the cold bath. To the resulting bright orange solution was added ca. 2 g of silica gel, and the solvent was removed at water aspirator pressure on a rotary evaporator. The residue was transferred to the top of a column filled with silica gel and separated by flash chromatography. The product appeared as a bright orange band that was collected in a round-bottom flask. The solvent was removed with a rotary evaporator to give pure product. The products were stored in a freezer (–20 °C) until use, to minimize decomposition–oxidation. Most of these complexes began to decompose at room temperature within minutes of their preparation and acceptable elemental analyses could not be obtained.

Pentacarbonyl[(methyl)(2-propen-1-oxy)carbene]chromium(0) (14a). From 1.00 g (3.20 mmol) of **13**, 0.40 g (3.20 mmol) of acetyl bromide, and 0.18 g (3.20 mmol) of allyl alcohol with purification by flash chromatography [hexane/EtOAc (9:1)], 0.50 g (1.80 mmol, 56%) of **14a** was obtained as an orange oil: ^{1}H NMR (300 MHz, $CDCl_3$, broad signals) δ 6.30 (s, 1 H), 5.40 (s, 4 H), 3.00 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 358.24 (Cr=C), 223.36 (*trans*-CO), 216.45 (4C, *cis*-CO), 132.67 (C2), 118.53 (C3), 80.13 (C1), 33.61 (Me); IR (film) ν 2064 (*trans*-CO), 1918 (br, *cis*-CO) cm^{-1}.

Pentacarbonyl[(3-buten-1-oxy)(methyl)carbene]chromium(0) (14b). From 2.00 g (6.40 mmol) of **13**, 0.79 g (6.40 mmol) of acetyl bromide, and 0.46 g (6.40 mmol) of 3-buten-1-ol after chromatography (hexane/EtOAc, 9:1), 1.30 g (4.50 mmol, 70%) of **14b** was obtained as an orange oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (tdd, 1 H, J = 17.1, 10.3, 6.8 Hz, H-3), 5.20 (overlapping m, 2 H, H-4), 4.96 (br s, 2 H, H-1), 2.93 (s, 3 H, Me), 2.73 (tq, 2 H, J = 6.6, 1.2 Hz, H-2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 358.24 (Cr=C), 223.33 (*trans*-CO), 216.44 (4 C, *cis*-CO), 132.66 (C3), 118.48 (C4), 79.77 (C1), 49.18 (Me), 33.57 (C2); IR (film) ν 2060 (*trans*-CO), 1950 (br, *cis*-CO) cm^{-1}; MS (CI, NH_3) 99 (M – $Cr(CO)_5$ + H^+).

Pentacarbonyl[(methyl)(3-methyl-3-buten-1-oxy)carbene]chromium(0) (14c). From 3.09 g (10.00 mmol) of **13**, 1.50 mL (12.00 mmol) of pivaloyl chloride, and 1.03 g (12.00 mmol) of 3-methyl-3-buten-1-ol after chromatography (petroleum ether), 1.39 g (4.60 mmol, 46%) of **14c** was

obtained as an orange oil: ^{1}H NMR (270 MHz, $CDCl_3$, broad signals) δ 4.90 (m, 4 H, H-4, H-2), 2.94 (s, 3 H, Cr=CMe), 2.70 (s, 2 H, H-2), 1.84 (s, 3 H, Me-C3); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 358.28 (Cr=C), 223.34 (*trans*-CO), 216.50 (4C, *cis*-CO), 140.49 (C3), 113.23 (C4), 78.98 (C1), 48.53 (Cr=C*Me*), 37.17 (Me-C3), 22.47 (C2); IR (film) ν 2050 (*trans*-CO), 1920 (br, *cis*-CO) cm^{-1}; MS (Cl, NH_3) 113 (M - $Cr(CO)_5$ + H^+).

Pentacarbonyl[(*trans*-3-hexen-1-oxy)(methyl)carbene]chromium(0) (14d). From 3.09 g (10.00 mmol) of **13**, 1.50 mL (12.00 mmol) of pivaloyl chloride, and 1.20 g (12.00 mmol) of *trans*-3-hexen-1-ol after flash chromatography (petroleum ether), 2.70 g (8.50 mmol, 85%) of **14d** was obtained as an orange oil: ^{1}H NMR (300 MHz, $CDCl_3$, broad signals) δ 5.69 (m, 1 H, C=CH), 5.48 (m, 1 H, C=CH), 4.91 (s, 2 H, H-1), 2.94 (s, 3 H, Cr=C*Me*), 2.68 (d, 2 H, J = 6.0 Hz), 2.07 (t, 2 H, J = 6.3 Hz), 1.01 (t, 3 H, J = 7.2 Hz, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) δ 357.58 (Cr=C), 223.45 (*trans*-CO), 216.48 (4 C, *cis*-CO), 136.44, 122.74, 80.87 (C1), 49.07 (Me), 32.51, 25.59, 13.48 (C6); IR (film) ν 2040 (*trans*-CO), 1915 (*cis*-CO) cm^{-1}; MS (CI, NH_3) 127 (M - $Cr(CO)_5$ + H^+).

Pentacarbonyl[(*cis*-3-hexen-1-oxy)(methyl)carbene]chromium(0) (14e). From 3.09 g (10.00 mmol) of **13**, 1.50 mL (12.00 mmol) of pivaloyl chloride, and 1.20 g (12.00 mmol) of *cis*-3-hexen-1-ol after flash chromatography (petroleum ether), 2.47 g (7.80 mmol, 78%) of **14e** was obtained as an orange oil: ^{1}H NMR (300 MHz, $CDCl_3$, broad signals) δ 5.47 (s, 2 H), 4.89 (s, 2 H), 2.91 (s, 4 H), 2.10 (s, 3 H), 1.00 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 357.74 (Cr=C), 223.35 (*trans*-CO), 216.43 (4 C, *cis*-CO), 135.58, 122.38, 80.75 (C1), 49.28 (Cr=C*Me*), 27.29, 20.62, 14.00 (C6); IR (film) ν 2045 (*trans*-CO), 1925 (br, *cis*-CO) cm^{-1}; MS (CI, NH_3) 144 (M - $Cr(CO)_5$ + NH_4^+), 127 (M - $Cr(CO)_5$ + H^+).

Pentacarbonyl[(methyl)(4-penten-2-oxy)carbene]chromium(0) (14f). From 3.09 g (10.00 mol) of **13**, 1.50 mL (12.00 mmol) of pivaloyl chloride, and 1.03 g (12.00 mmol) of 4-penten-2-ol after chromatography (petroleum ether), 1.99 g (6.60 mmol, 66%) of **14f** was obtained as an orange oil: ^{1}H NMR (300 MHz, $CDCl_3$, broad signals) δ 5.81 (m, 2 H, H-2, H-4), 5.18 (s, 2 H, H-5), 2.92 (s, 3 H, Cr=CMe), 2.61 (s, 2 H, H-3), 1.53 (s, 3 H, Me-C2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 353.30 (Cr=C), 223.35 (*trans*-CO), 216.47 (4 C, *cis*-CO), 131.89 (C4), 119.33 (C5), 89.24 (C2), 50.04 (Cr=C*Me*), 40.71 (C3), 19.98 (C1); IR (film) ν 2062 (*trans*-CO), 1916 (*cis*-CO, br) cm^{-1}; MS (CI, NH_3) 113 (M - $Cr(CO)_5$ + H^+).

Pentacarbonyl[(methyl)(4-methyl-3-penten-1-oxy)carbene]chromium(0) (14g). From 1.55 g (5.00 mmol) of **13**, 0.39 mL (5.00 mmol) of acetyl bromide, and 0.46 g (4.60 mmol) of 4-methyl-3-penten-1-ol after chromatography (hexane), 0.94 g (3.00 mmol, 64%) of **14g** was obtained as an orange oil: ^{1}H NMR (300 MHz, $CDCl_3$, broad signals) δ 4.80 (s, 1 H, H-3), 4.48 (s, 2 H, H-1), 2.52 (s, 3 H, Cr=CMe), 2.28 (s, 2 H, H-2), 1.34 (s, 6 H, C=CMe_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 357.47 (Cr=C), 223.48 (*trans*-CO), 216.50 (4 C, *cis*-CO), 135.93 (C3), 118.00 (C4), 80.89 (C1), 49.68 (Cr=C*Me*), 28.27 (C2), 25.68 (Me), 17.80 (Me); IR (film) ν 2025 (*trans*-CO), 1920 (br, *cis*-CO) cm^{-1}; MS (CI, NH_3) (M - $Cr(CO)_5$ + H^+).

Pentacarbonyl[(methyl)(4-penten-1-oxy)carbene]chromium(0) (14h). From 3.09 g (10.00 mmol) of **13**, 1.50 mL (12.00 mmol) of pivaloyl chloride, and 1.03 g (12.00 mmol) of 4-penten-1-ol after chromatography (petroleum ether/Et_2O, 9:1), 2.08 g of an orange oil was obtained. The oil was dissolved in 50 mL of petroleum ether, washed with 2 × 75 mL of 1 M $NaHCO_3$ (aqueous) to remove pivalic acid, and dried with $MgSO_4$ to give, after solvent removal, 1.87 g (6.10 mmol, 61%) of **14h** as an orange oil: ^{1}H NMR (300 MHz, $CDCl_3$, broad signals) δ 5.83 (m, 1 H, H-4), 5.12–4.80 (overlapping m, 4 H, H-1, H-5), 2.94 (s, 3 H, Cr=CMe), 2.30 (m, 2 H, H-3), 2.10 (m, 2 H, H-2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 357.95 (Cr=C), 223.38 (*trans*-CO), 216.47 (4 C, *cis*-CO), 136.63 (C4), 116.07 (C5), 80.28 (C1), 49.13 (Cr=C*Me*), 29.87, 28.36; IR (film) ν (*trans*-CO), 1916 (br, *cis*-CO) cm^{-1}; MS (Cl, NH_3) 113 (M - $Cr(CO)_5$ + H^+).

Pentacarbonyl[[[*trans*-2-(2-propenyl)cyclohexyl]oxy](methyl)carbene]chromium(0) (14i). From 3.09 g (10.00 mmol) of **13**, 0.85 g (11.00 mmol) of acetyl bromide, and 1.68 g (12.00 mmol) of *trans*-2-(2-propenyl)-1-cyclohexanol after flash chromatography (hexane), 1.65 g (4.60 mmol, 46%) of **14i** was obtained as an orange oil that slowly crystallized to yellow needles: mp 35–37 °C, ^{1}H NMR (300 MHz, $CDCl_3$, broad signals) δ 5.71 (s, 1 H, C*H*=CH_2), 5.03 (s, 3 H, H-1, CH=CH_2), 2.92 (s, 3 H, Cr=CMe), 2.25–1.15 (m, 11 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 353.90 (Cr=C), 223.25 (*trans*-CO), 216.62 (4 C, *cis*-CO), 136.44 (*C*H=CH_2), 116.26 (CH=*C*H_2), 96.01 (C1), 50.24 (Cr=C*Me*), 42.32, 36.56, 32.73, 30.01, 24.66, 23.95; IR (film) ν 2060 (*trans*-CO), 1935 (br, *cis*-CO) cm^{-1}. Anal. ($C_{16}H_{18}CrO_6$) C, H.

Pentacarbonyl[(1,5-hexadien-3-oxy)(methyl)carbene]chromium(0) (14j). From 1.55 g (5.00 mmol) of **13**, 0.75 mL (6.00 mmol) of pivaloyl chloride, and 0.59 g (6.0 mmol) of 1,5-hexadien-3-ol, after flash chromatography (petroleum ether), 0.87 g (2.80 mmol, 56%) of **14j** was obtained as an orange oil: ^{1}H NMR (300 MHz, $CDCl_3$, broad signals) δ 6.0 (s, 1 H), 5.8 (s, 1 H), 5.2 (s, 5 H), 2.96 (s, 3 H, Cr=CMe), 2.70 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 355.97 (Cr=C), 223.51 (*trans*-CO), 216.36 (4 C, *cis*-CO), 134.43, 131.47, 119.61, 118.02, 91.72 (C3), 49.80 (Cr=C*Me*), 39.60 (C4); IR (film) ν 2062 (*trans*-CO), 1921 (br, *cis*-CO) cm^{-1}; MS (Cl, NH_3) 125 (M - $Cr(CO)_5$ + H^+).

Pentacarbonyl[(3-hexyn-1-oxy)methyl)carbene]chromium(0) (14k). From 1.55 g (5.00 mmol) of **13**, 0.75 mL (6.00 mmol) of pivaloyl chloride, and 0.59 g (6.00 mmol) of 3-hexyn-1-ol after flash chromatography (petroleum ether/Et_2O, 9:1), 1.51 g of an orange oil was obtained. The oil was rechromatographed, to remove pivalic acid, eluting with petroleum ether to give 0.82 g (2.60 mmol, 52%) of **14h** as an orange oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.95 (br s, 2 H, H-1), 2.97 (s, 3 H, Cr=CMe), 2.85 (tt, 2 H, $J_{2,1}$ = 6.5, $J_{2,5}$ = 2.3 Hz, H-2), 2.16 (tq, 2 H, $J_{5,6}$ = 7.5, $J_{5,2}$ = 2.4 Hz, H-5), 1.10 (t, 3 H, $J_{6,5}$ = 7.6 Hz, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) δ 358.76 (Cr=C), 223.35 (*trans*-CO), 216.29 (4 C, *cis*-CO), 84.56, 78.56 (C1), 73.61, 48.97 (Cr=C*Me*), 20.04, 13.88, 12.29; IR (film) ν 2050 (*trans*-CO), 1920 (br, *cis*-CO) cm^{-1}; MS (CI, NH_3) 125 (M - $Cr(CO)_5$ + H^+).

Pentacarbonyl[(methyl)(4-pentyn-1-oxy)carbene]chromium(0) (14l). From 3.09 g (10.00 mmol) of **13**, 1.50 mL (12.00 mmol) of pivaloyl chloride, and 1.01 g (12.00 mmol) of 4-pentyn-1-ol after flash chromatography (petroleum ether/Et_2O, 9:1), 2.26 g of an orange oil was obtained. The oil was rechromatographed to remove pivalic acid (petroleum ether) yielding 1.91 g (6.30 mmol, 63%) of **14l** as an orange oil: ^{1}H NMR (300 MHz, $CDCl_3$), δ 4.99 (br s, 2 H, H-1), 2.95 (s, 3 H, Cr=CMe), 2.46 (dt, 2 H, $J_{3,2}$ = 6.7, $J_{3,5}$ = 2.3 Hz, H-3), 2.20 (quin, 2 H, $J_{2,1}$ = $J_{2,3}$ = 6.4 Hz, H-2), 2.02 (t, 1 H, $J_{5,4}$ = 2.5 Hz, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 358.72 (Cr=C), 223.37 (*trans*-CO), 216.35 (4 C, *cis*-CO), 81.99 (C4), 79.06 (C1), 69.86 (C5), 49.29 (Cr=C*Me*), 27.95, 26.88; IR (film) ν 3311 (C≡C—H), 2063 (*trans*-CO), 1942 (br, *cis*-CO) cm^{-1}.

Pentacarbonyl[(methyl)(10-undecen-1-oxy)carbene]chromium(0) (14m). From 3.09 g (10.00 mmol) of **13**, 1.50 mL (12.00 mmol) of pivaloyl chloride, and 2.04 g (12.00 mmol) of 10-undecen-1-ol after chromatography (petroleum ether), 2.86 g (7.40 mmol, 74%) of **14m** was obtained as an orange oil: ^{1}H NMR (300 MHz, $CDCl_3$, broad signals) δ 5.80 (s, 1 H, H-10), 4.94 (s, 4 H, H-1, H-11), 2.92 (s, 3 H, Cr=CMe), 2.00 (s, 4 H), 1.32 (s, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 357.33 (Cr=C), 223.36 (*trans*-CO), 216.49 (4 C, *cis*-CO), 139.04 (C10), 114.08 (C11), 81.70 (C1), 49.51 (Cr=C*Me*), 33.74, 29.27 (6C), 25.78; IR (film) ν 2062 (*trans*-CO), 1922 (*cis*-CO) cm^{-1}.

Pentacarbonyl[(3-cyclohexen-1-ylmethyl)oxy](methyl)carbene]chromium(0) (14n). From 1.55 g (5.00 mmol) of **13**, 0.43 mL (5.50 mmol) of acetyl bromide, and 0.67 g (6.00 mmol) of 3-cyclohexene-1-methanol after flash chromatography (hexane), 0.44 g (1.30 mmol, 26%) of **14n** was obtained as an orange oil: ^{1}H NMR (300 MHz, $CDCl_3$, broad signals) δ 5.72 (s, 2 H, CH=CH), 4.78 (s, 2 H, OCH_2), 2.95 (s, 3 H, Cr=CMe), 2.29 (s, 2 H), 2.14 (s, 2 H), 1.93 (s, 2 H), 1.52 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 357.80 (Cr=C), 223.41 (*trans*-CO), 216.52 (4 C, *cis*-CO), 127.15, 125.04, 85.54 (C1), 49.61 (Cr=C*Me*), 33.84, 27.90, 25.11, 24.24; IR (film) ν 2062 (*trans*-CO), 1921 (br, *cis*-CO) cm^{-1}.

General Procedure for the Preparation of Bicyclic Cyclobutanones 15. In an oven-dried Fischer Porter pressure vessel was placed a ~0.1 M yellow solution of the carbene in diethyl ether or acetonitrile. The vessel was saturated with CO—three cycles to 90–100 psi of CO—and irradiated (450-W Hanovia lamp) for ~24 h under 90 psi of CO. The now colorless solution was removed with a pipet to leave crystalline $Cr(CO)_6$ and some green precipitate. The solvent was removed on a rotary evaporator at water aspirator pressure to give a white semisolid composed of product and $Cr(CO)_6$. The crude material was triturated with a few milliliters of petroleum ether, the solution was put on top of a column and flash chromatographed by elution with first petroleum ether and then a mixture of petroleum ether/Et_2O, to give, after solvent removal on a rotary evaporator, the pure cyclobutanone.

1-Methyl-2-oxabicyclo[3.2.0]heptan-7-one (15b). From irradiation of 1.20 g (4.13 mmol) of **14b** in 30 mL of Et_2O at 90 psi of CO for 23.5 h after chromatography (petroleum ether/Et_2O, 1:1, 50 mL), 0.46 g (3.65 mmol, 88%) of **15b** was obtained as a colorless oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.19 (t, 1 H, $J_{3,3'}$ = $J_{3,4}$ = 8.7 Hz, H-3), 3.76 (ddd, 1 H, $J_{3',4}$ = 11.7, $J_{3',3}$ = 9.4, $J_{3',4'}$ = 5.5 Hz, H-3'), 3.11 (dd, 1 H, $J_{6,6'}$ = 18.6, $J_{6,5}$ = 9.6 Hz, H-6), 2.67 (dt, 1 H, $J_{5,4}$ = $J_{5,6}$ = 8.8, $J_{5,6'}$ = 4.9 Hz, H-5), 2.44 (dd, 1 H, $J_{6',6}$ = 18.6, $J_{6',5}$ = 4.9 Hz, H-6'), 2.10 (tt, 1 H, $J_{4,3'}$ = $J_{4,4'}$ = 12.2, $J_{4,3}$ = $J_{4,5}$ = 7.9 Hz, H-4), 1.87 (dd, 1 H, $J_{4',4}$ = 12.7, $J_{4',3'}$ = 5.4 Hz, H-4'), 1.37 (s, 3 H, Me); ^{13}C NMR (70 MHz, $CDCl_3$) δ 213.44 (CO), 100.41 (C1), 68.93 (C3), 47.51 (C6), 36.38 (C5), 32.44 (C4), 15.97 (Me); IR (film) ν 1775 (CO) cm^{-1}; MS (CI, NH_3) 144 (M +

NH_4^+), 127 (M + H^+); MS (EI) 98 (M^+ - CO), 84 (M^+ - CH=C=O). Anal. ($C_7H_{10}O_2$) C, H.

1,5-Dimethyl-2-oxabicyclo[3.2.0]heptan-7-one (15c). From irradiation of 841 mg (2.77 mmol) of **14c** in 25 mL of Et_2O at 90 psi of CO for 30 h after flash chromatography (petroleum ether/Et_2O, 8:2), 240 mg (1.71 mmol, 62%) of **15c** was obtained as a colorless oil. Spectral data was in complete accordance with literature values.[20]

***exo*-6-Ethyl-1-methyl-2-oxabicyclo[3.2.0]heptan-7-one (15d).** Irradiation of 1.27 g (4.00 mmol) of **14d** for 19 h, after flash chromatography (petroleum ether/Et_2O, 9:1), gave 0.29 g (1.89 mmol, 47%) of **15d** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.22 (t, 1 H, $J_{3,3'} = J_{3,4}$ = 8.6 Hz, H-3), 3.78 (ddd, 1 H, $J_{3',4} = 11.7$, $J_{3',3} = 9.7$, $J_{3',4'} = 5.4$ Hz, H-3'), 2.56 (ddd, 1 H, $J_{6,CH_2'} = 7.0$, $J_{6,5} = 5.2$ Hz, H-6), 2.37 (dd, 1 H, $J_{5,4} = 7.5$, $J_{5,6} = 5.2$ Hz, H-5), 2.11 (tt, 1 H, $J_{4,3'} = J_{4,4'} = 12.1$, $J_{4,3} = J_{4,5} = 7.8$ Hz, H-4), 1.91 (dd, 1 H, $J_{4',4} = 12.5$, $J_{4',3'} = 5.4$ Hz, H-4'), 1.71 (apparent octet, 1 H, J = 7.2 Hz, CH_2CH_3), 1.59 (m, 1 H, CH_2CH_3), 1.37 (s, 3 H, MeC1), 0.97 (t, 3 H, J = 7.4 Hz, CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.47 (CO), 98.01 (C1), 69.23 (C3), 62.98 (C6), 43.26 (C5), 32.69 (C4), 23.06 (CH_2), 16.81 (*Me*-C5), 11.87 (CH_2CH_3); IR (film) ν 1775 (CO) cm^{-1}; MS (CI, NH_3) 172 (M + NH_4^+), 155 (M + H^+). Anal. ($C_9H_{14}O_2$) C, H.

***endo*-7-Ethyl-1-methyl-2-oxabicyclo[3.1.1]heptan-6-one (15e') and *endo*-6-Ethyl-1-methyl-2-oxabicyclo[3.2.0]heptan-7-one (15e).** From 1.27 g (4.00 mmol) of **14e** after irradiation for 22.5 h and flash chromatography (petroleum ether/Et_2O, 9:1), 137 mg (0.64 mmol, 22%) of **15e'** followed by 181 mg (0.84 mmol, 29%) of **15e** was obtained as colorless oils. Cyclobutanone **15e'**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.99 (dd, 1 H, $J_{3,4'} = 11.5$, $J_{3,4} = 7.5$ Hz, H-3), 3.82 (dt, 1 H, $J_{3',3} = J_{3',4} = 11.7$, $J_{3',4'} = 5.8$ Hz, H-3'), 3.22 (t, 1 H, $J_{5,4} = J_{5,7} = 5.7$ Hz, H-5), 2.50 (dt, 1 H, $J_{4,3'} = J_{4,4'} = 12.4$, $J_{4,3} = 7.6$ Hz, H-4), 1.96 (td, 1 H, $J_{4',4} = 12.5$, $J_{4',3'} = J_{4',5} = 6.2$ Hz, H-4'), 1.83–1.64 (m, 3 H, H-7, CH_2), 1.21 (s, 3 H, Me-C1), 0.99 (t, 3 H, J = 6.9 Hz, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.36 (CO), 95.15 (C1), 63.67 (C3), 57.89 (C5), 41.76 (C7), 26.77 (C4), 16.74, 15.37, 12.38; IR (film) ν 1776 (CO) cm^{-1}; MS (CI, NH_3) 172 (M + NH_4^+), 155 (M + H^+). Anal. ($C_9H_{14}O_2$) C, H.

Cyclobutanone **15e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.10 (t, 1 H, $J_{3,3'} = J_{3,4} = 8.7$ Hz, H-3), 3.55 (ddd, 1 H, $J_{3',4} = 11.4$, $J_{3',3} = 9.5$, $J_{3',4'} = 6.0$ Hz, H-3'), 3.04 (ddd, 1 H, $J_{6,5} = 10.4$, $J_{6,CH_2} = 8.6$, $J_{6,CH_2'} = 7.2$ Hz, H-6), 2.71 (t, 1 H, $J_{5,6} = J_{5,4} = 9.7$ Hz, H-5), 1.99 (m, 1 H, H-4), 1.87 (dd, 1 H, $J_{4',4} = 13.2$, $J_{4',3'} = 5.9$ Hz, H-4'), 1.62 (septet, 1 H, J = 7.3 Hz, CH_2), 1.42 (s, 3 H, MeC1), 1.32 (septet, 1 H, J = 7.4 Hz, CH_2'), 0.95 (t, 3 H, J = 7.4 Hz, CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 217.27 (CO), 98.32 (C1), 69.66 (C3), 56.84 (C6), 39.92 (C5), 26.47, 16.32 (2 C), 12.32; IR (film) ν 1782 (CO) cm^{-1}; MS (CI, NH_3) 172 (M + NH_4^+). 155 (M + H^+). Anal. ($C_9H_{14}O_2$) C, H.

1,3-Dimethyl-2-oxabicyclo[3.2.0]heptan-7-one (15f). From 912 mg (3.00 mmol) of **14f** after irradiation for 20 h and flash chromatography (petroleum ether/Et_2O, 9:1), 242 mg (1.86 mmol, 62%, endo/exo, 11:1) of **15f** was obtained as a colorless oil. *endo*-**15f** (from an 11:1 mixture): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.45 (sextet, 1 H, $J_{3,4} = J_{3,4'} = J_{3,Me}$ = 6.5 Hz, H-3), 3.17 (m, 1 H, H-6), 2.82–2.69 (m, 2 H, H-5, H-6'), 2.51 (ddd, 1 H, $J_{4,4'} = 13.1$, $J_{4,5} = 9.0$, $J_{4,3} = 6.5$ Hz, H-4), 1.61 (ddd, 1 H, $J_{4',4} = 13.1$, $J_{4',5} = 7.2$, $J_{4',3} = 6.5$ Hz, H-4'), 1.38 (s, 3 H, MeC1), 1.28 (d, 3 H, $J_{Me,3} = 6.4$ Hz, Me–C3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.58 (CO), 100.64 (C1), 80.15 (C3), 48.62 (C6), 41.37 (C5), 37.31 (C4), 21.55 (Me), 16.41 (Me); IR (film) ν 1783 (CO) cm^{-1}; MS (CI, NH_3) 158 (M + NH_4^+), 141 (M + H^+). Anal. ($C_8H_{14}O_2$) C, H.

exo-**15**; (partial spectra from an 11:1 mixture): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.13 (sept, 1 H, $J_{3,4} = 11.4$, $J_{3,4'} = J_{3,Me} = 5.7$ Hz, H-3), 2.01 (dd, 1 H, $J_{4,4'} = 12.7$, $J_{4,3} = 4.7$ Hz, H-4), 1.74 (m, 1 H, H-4'), 1.40 (s, 3 H, Me-C1), 1.33 (d, 3 H, $J_{Me,3} = 5.9$ Hz, Me-C3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.01 (CO), 99.92 (C1), 75.77 (C3), 48.41 (C6), 39.89 (C5), 37.05 (C4), 19.54 (Me), 16.01 (Me).

1,7,7-Trimethyl-2-oxabicyclo[3.1.1]heptan-6-one (15g). Irradiation of 0.32 g (1.00 mmol) of **14g**, after chromatography (petroleum ether/Et_2O, 9:1), gave 0.12 g (0.80 mmol, 80%) of **15g** as white crystals: ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.00 (dd, 1 H, $J_{3,3'} = 11.5$, $J_{3,4} = 7.7$ Hz, H-3), 3.82 (dt, 1 H, $J_{3'3} = J_{3',4} = 11.6$, $J_{3',4'} = 6.0$ Hz, H-3'), 2.80 (d, 1 H, $J_{5,4'}$ = 5.7 Hz, H-5), 2.59 (dt, 1 H, $J_{4,4'} = J_{4,3'} = 12.6$, $J_{4,3} = 7.8$ Hz, H-4), 2.06 (td, 1 H, $J_{4'4} = 12.5$, $J_{4',3} = J_{4',5} = 6.1$ Hz, H-4'), 1.21 (s, 3 H, Me), 1.05 (s, 3 H, Me), 1.00 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.58 (CO), 95.30 (C1), 63.89 (C3), 62.63 (C5), 35.55 (C7), 29.60 (C4), 29.13, 14.08, 11.90; IR (film) ν 1780 (CO) cm^{-1}; MS (CI, NH_3) 155 (M + H^+). Anal. ($C_9H_{14}O_2$) C, H.

1-Methyl-2-oxabicyclo[4.2.0]octan-8-one (15h). Irradiation of 1.22 g (4.00 mmol) of **14h** for 24 h, after chromatography (petroleum ether/Et_2O, 9:1) gave 0.41 g (2.93 mmol, 73%) of **15h** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.74 (m, 1 H, H-3), 3.58 (m, 1 H, H-3'), 2.95 (dd, 1 H, $J_{7,7'} = 16.5$, $J_{7,6} = 8.8$ Hz, H-7), 2.43 (dd, 1 H, $J_{7',7} = 16.6$, $J_{7',6} = 3.9$ Hz, H-7'), 2.21 (m, 2 H, H-5, H-6), 1.50 (m, 2 H, H-4), 1.37 (m, 1 H, H-5'), 1.35 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.05 (CO), 88.35 (C1), 64.33 (C3), 47.43 (C6), 29.79, 26.14, 21.57 (Me), 21.48; IR (film) ν 1780 (CO) cm^{-1}; high-resolution mass spectrum calcd for $C_8H_{12}O_2$ 140.0837, found 140.0841.

Cyclobutanone (15h) and 1-Methyl-2,9-dioxabicyclo[4.3.0]nonan-8-one. A solution of 0.30 g (1.00 mmol) of **14h** in MeCN was irradiated for 15 h as described in the general procedure but in the absence of CO. The solvent was removed on a rotary evaporator at water aspirator pressure to give a yellow solid. The solid was dissolved in EtOAc and filtered through Celite, and the solution was diluted with one volume of hexane. The mixture was air oxidized in a light box (6 × 20 W Vitalite fluorescent bulbs) for 40 h. The brown precipitate was removed by filtration, and the solvent was removed on a rotary evaporator to give 0.15 g of a pale yellow oil. Flash chromatography eluting with hexane/EtOAc (8:2) gave first 0.06 g (0.43 mmol, 43%) of **15h** followed by 0.3 g (0.19 mmol, 19%) of 1-methyl-2,9-dioxabicyclo[4.3.0]nonan-8-one both as colorless oils. The latter has the following spectral data: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.74 (m, 2 H, H-3), 2.69 (dd, 1 H, $J_{7,7'} = 17.2$, $J_{7,6} = 7.4$ Hz, H-7), 2.38 (dd, 1 H, $J_{7',7} = 17.2$, $J_{7',1} = 4.2$ Hz, H-7'), 2.28 (m, 1 H), 1.91 (m, 1 H), 1.59 (m, 3 H), 1.53 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.42 (CO), 107.51 (C1), 62.73 (C3), 37.36 (C6), 36.39 (C7), 24.92, 24.48 (Me), 21.28; IR (film) ν 1771 (CO) cm^{-1}; high-resolution mass spectrum calcd for $C_8H_{12}O_3$ 156.0786, found 156.0793.

Tricyclic Ketones 15i and 15i'. A 359-mg portion (1.00 mmol) of **14i** was irradiated for 23.5 h at 90 psi of CO as described in the general procedure. The solvent was removed on a rotary evaporator to give a white semisolid that was triturated with a few milliliters of EtOH (100%) and filtered through a 0.5-cm-thick Celite pad. Removal of solvent on a rotary evaporator gave 189 mg (0.97 mmol, 97%) of a 2:1 mixture **15i** and **15i'** as an almost colorless oil. Data from a ca. 65:35 mixture: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.27 (dd, 1 H, J = 16.7, 10.0 Hz), 3.03 (m, 2 H), 2.95 (dd, 1 H, J = 16.1, 7.9 Hz), 2.85 (dd, 1 H, J = 16.7, 9.3 Hz), 2.24 (m, 3 H), 2.11 (dd, 1 H, J = 15.9, 1.8 Hz), 1.9–1.4 (m, 11 H), 1.38 (s, 3 H, Me), 1.28–0.77 (m, 10 H), superimposed on 1.23 (s, 3 H, Me); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 209.79 (CO), 204.22 (CO), 89.39, 88.58, 77.71, 75.75, 47.96, 46.94, 37.25, 35.79, 35.12, 32.58, 32.47, 31.78, 31.68, 31.33, 30.24, 29.72, 25.55, 25.46, 24.91, 24.56, 23.28, 16.54; IR (film) ν 1785 (CO) cm^{-1}; MS (EI): 194 (M^+). Anal. ($C_{12}H_{18}O_2$) C, H. Found: C, 74.37; H, 9.17.

5-Methyl-1-phenyl-2-oxabicyclo[3.1.0]hexane (17). Carbon monoxide was bubbled through a solution of 714 mg (1.92 mmol) of pentacarbonyl[[(tetramethylammonio)oxy](phenyl)carbene]chromium(0) in 25 mL of CH_2Cl_2 for 15 min, the solution was cooled to −40 °C put under CO atmosphere, and 295 μL (2.40 mmol) of pivaloyl chloride was added by syringe. After 1 h at −35 ± 5 °C, 206 mg (2.40 mmol) of 3-methyl-3-buten-1-ol in 6 mL of CH_2Cl_2 was added by syringe and the vessel was pressurized to 90 psi of CO. The reaction mixture was allowed to warm to room temperature overnight (15 h) and was then irradiated under 90 psi of CO for 24 h. Evaporation of the solvent, on a rotary evaporator, from the yellow solution gave a yellow solid–oil. The precipitate was triturated with petroleum ether and filtered through Celite to give, after solvent removal, 607 mg of a pale green oil with some solid $Cr(CO)_6$. The oil was purified by radial chromatography (2-mm plate, petroleum ether/Et_2O, 95:5) to give, after solvent removal, 407 mg of a colorless oil. The oil was rechromatographed on a 16 × 2.5 cm column eluting with first petroleum ether (40 mL) followed by petroleum ether/Et_2O (9:1) to give, after solvent removal, 279 mg (1.60 mmol, 83%) of **17** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.3 (m, 5 H, ArH), 4.16 (dt, 1 H, $J_{3,3'} = J_{3,4} = 8.7$, $J_{3,4'} = 3.1$ Hz, H-3), 3.60 (td, 1 H, $J_{3',4'} = J_{3',3} = 9.6$, $J_{3',4} = 7.8$ Hz, H-3'), 2.09 (m, 2 H, H-4), 1.34 (d, 1 H, $J_{6,6'} = 6.6$ Hz, H-6), 1.01 (s, 3 H, Me), overlapping 1.00 (d, 1 H, H-6'); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.51 (ipso), 127.86, 127.12, 126.84, 72.58 (C1), 65.49 (C3), 35.75 (C4), 29.06 (C5), 17.90, 17.64; IR (film) ν 3063, 3029, 2944, 2868, 1449, 1128, 1070, 1041, 1027, 765, 698 cm^{-1}; MS (CI, NH_3) 192 (M + NH_4^+), 175 (M + H^+). Anal. ($C_{12}H_{14}O$) C, H.

Pentacarbonyl[(cyclopropyl)(3-methyl-3-buten-1-oxy)carbene]chromium(0) (18). Similar treatment of 1.68 g (5.00 mmol) of pentacarbonyl[(cyclopropyl)[tetramethylammonio)oxy]carbene]chromium(0) with first 0.75 mL (6.00 mmol) of pivaloyl chloride in 150 mL of CH_2Cl_2 for 80 min at −35 °C and then 0.52 g (6.00 mmol) of 3-methyl-3-buten-1-ol in 6 mL of CH_2Cl_2 for 2 h followed by slow warming to room temperature (17 h) as described in the general procedure gave, after flash chromatography (13 × 2.5 cm column, petroleum ether), 1.16 g (3.52 mmol, 70%) of **18** as an orange oil that crystallized when stored in freezer (−18 °C): mp <20 °C; ^{1}H NMR (300 MHz, $CDCl_3$, broad signals) δ 5.01 (s, 2 H, H-1), 4.91 (s, 1 H, H-4), 4.82 (s, 1 H, H-4'), 3.46 (s, 1 H, cyclopropyl-CH), 2.62 (s, 2 H, H-2), 1.82 (s, 3 H, Me-C3), 1.39 (s, 2 H, cyclopropyl-CH_2), 1.18 (s, 2 H, cyclopropyl-CH_2); ^{13}C NMR (300 MHz, $CDCl_3$) δ 351.34 (Cr=C), 223.55 (*trans*-CO), 216.81 (4 C, *cis*-

CO), 140.65 (C4), 113.14 (C3), 78.06 (C1), 41.54, 37.25, 22.11, 17.91 (2 C); IR (film) ν 2060 (*trans*-CO), 1917 (br, *cis*-CO); MS (CI, NH_3) 139 (M - $Cr(CO)_5$ + H^+).

Pentacarbonyl[(benzyl)(3-methyl-3-buten-1-oxy)carbene]chromium(0) (19). Reaction of 1.93 g (5.00 mmol) of pentacarbonyl[(benzyl)[(tetramethylammonio)oxy]carbene]chromium(0) with first 0.45 mL (6.00 mmol) of acetyl bromide in 75 mL of CH_2Cl_2 for 1 h at -35 °C and 0.52 g (6.00 mmol) of 3-methyl-3-buten-1-ol in 6 mL of CH_2Cl_2 as described in the general procedure. After standard isolation by flash chromatography (petroleum ether) an orange oil (1.01 g) was obtained. The oil was rechromatographed (petroleum ether/Et_2O, 95:5) to give 0.38 g (1.00 mmol, 20%) of **19** as orange crystals: mp 43-45 °C; ^1H NMR (300 MHz, $CDCl_3$, broad peaks) δ 7.28 (s, 3 H, Ar), 7.14 (s, 2 H, Ar), 5.09 (s, 2 H, ArCH_2), 4.86 (s, 1 H, H-4), 4.72 (s, 1 H, H-4'), 4.59 (s, 2 H, H-1), 2.61 (s, 2 H, H-2), 1.74 (s, 3 H, Me-C3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 355.93 (Cr=C), 223.00 (*trans*-CO), 216.25 (4 C, *cis*-CO), 140.23, 134.84, 129.61, 128.45, 126.87, 113.32 (C4), 80.11 (C1), 68.27 (ArCH_2), 36.96 (C2), 22.26 (*Me*-C3); IR (film) ν 2062 (*trans*-CO), 1924 (br, *cis*-CO); MS (CI, NH_3) 206 (M - $Cr(CO)_5$ + NH_4^+), 189 (M - $Cr(CO)_5$ + H^+).

1-Cyclopropyl-5-methyl-2-oxabicyclo[3.2.0]heptan-7-one (20). Irradiation of 660 mg (2.00 mmol) of **18** for 22 h, after chromatography (petroleum ether/Et_2O, 1:1), gave 214 mg (1.29 mmol, 65%) of **20** as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 4.01 (ddd, 1 H, $J_{3,3'}$ = 9.4, $J_{3,4'}$ = 8.1, $J_{3,4}$ = 1.2 Hz, H-3), 3.57 (ddd, 1 H, $J_{3',4'}$ = 11.7, $J_{3',3}$ = 9.5, $J_{3',4}$ = 5.5 Hz, H-3'), 2.67 (dd, 1 H, $J_{6,6'}$ = 18.4, J = 0.8 Hz, H-6), 2.54 (d, 1 H, $J_{6',6}$ = 18.5 Hz, H-6'), 1.95 (ddd, 1 H, $J_{4,4'}$ = 11.6, $J_{4,3'}$ = 5.5, $J_{4,3}$ = 0.9 Hz, H-4), 1.77 (dt, 1 H, $J_{4',4}$ = $J_{4',3'}$ = 11.7, $J_{4',3}$ = 8.1 Hz, H-4'), 1.36 (s, 3 H, Me), 0.78 (tt, 1 H, J_1 = 8.2, J_2 = 5.3 Hz, cyclopropyl-CH), 0.43 (m, 3 H, cyclopropyl-CH_2), 0.22 (m, 1 H, cyclopropyl-CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.80 (CO), 108.10 (C1), 67.33 (C8), 54.89 (C6), 41.58 (C5), 39.98 (C4), 21.13 (Me), 7.89 (cyclopropyl), 0.55 (cyclopropyl), -0.29 (cyclopropyl); IR (film) ν 1776 cm^{-1}; MS (CI, NH_3) 167 (M + H^+). Anal. ($C_{10}H_{14}O_2$) C, H.

1-Benzyl-5-methyl-2-oxabicyclo[3.2.0]heptan-7-one (21). Irradiation of 380 mg (1.00 mmol) of **19** for 4 h gave, after chromatography (petroleum ether/Et_2O, 3:1), 205 mg (0.95 mmol, 95%) of **21** was white crystals: mp 51-52 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24 (m, 5 H, Ar), 4.14 (ddd, 1 H, $J_{3,3'}$ = 9.3, $J_{3,4'}$ = 8.3, $J_{3,4}$ = 0.9 Hz, H-3), 3.71 (ddd, 1 H, $J_{3',4'}$ = 11.7, $J_{3',3}$ = 9.6, $J_{3',4}$ = 5.6 Hz, H-3'), 3.06 (d, 1 H, J_{gem} = 14.8 Hz, ArCH_2), 2.84 (d, 1 H, J_{gem} = 14.9 Hz, ArCH_2), 2.78 (d, 1 H, $J_{6,6'}$ = 18.7 Hz, H-6), 2.69 (d, 1 H, $J_{6',6}$ = 18.4 Hz, H-6'), 1.99 (dd, 1 H, $J_{4,4'}$ = 12.4, $J_{4,3'}$ = 5.4 Hz, H-4), 1.76 (dt, 1 H, $J_{4',4}$ = $J_{4',3'}$ = 12.1, $J_{4',3}$ = 8.2 Hz, H-4'), 1.34 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.48 (CO), 135.53 (ipso), 130.03, 127.83, 126.27 (para), 100.07 (C1), 67.46 (C3), 54.69 (ArCH_2), 42.06 (C5), 39.72 (C6), 34.29 (C4), 21.09 (Me); IR (film) ν 1776 (CO) cm^{-1}; MS (CI, NH_3) 234 (M + NH_4^+), 217 (M + H^+). Anal. ($C_{13}H_{16}O_2$): C, H.

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A Concise Approach to Enantiomerically Pure Carbocyclic Ribose Analogues. Synthesis of (4*S*,5*R*,6*R*,7*R*)-7-(Hydroxymethyl)spiro[2.4]heptane-4,5,6-triol 7-*O*-(Dihydrogen phosphate)

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Abstract: This paper describes a synthesis of **5**, an analogue of 5-phospho-α-D-ribofuranose and instantiates a unique new approach to optically active carbocyclic analogues of ribofuranosides. The synthesis of **5** follows a general scheme that is outlined in brief retrosynthetic fashion in eq 1. The polyhydroxylated spiro[2.4]heptane (**5**) may be prepared via a suitably protected polyhydroxylated methylene cyclopentane **A**. The novelty of the synthetic approach described here is illustrated in the excision of the exocyclic methylene unit from the cyclopentanoid nucleus to generate a linear pentanose fragment (**B**) and a vinylidene fragment (**C**). In the forward direction, two carbon-carbon bonds are to be formed to the same carbon atom of this excised vinylidene fragment (**C**) and in this way two remote carbons on the pentanose skeleton **B** are "united" to form the methylenecyclopentane ring. The carbocyclic D-ribofuranose analogue **5** is prepared in seven steps and 7% overall yield from a D-ribofuranose starting material. The method is recommended to be generally serviceable for preparing carbocylic furanoside analogues.

The "carba" analogues of carbohydrates include carbocylic analogues, wherein the oxygen atom contained within the usual furanoid or pyranoid rings has been replaced with a carbon atom, and C-glycosides, wherein the anomeric oxygen atom has been replaced with a carbon atom.[1] While carbocylic carbohydrate analogues, for example, aristeromycin (**1**)[2] and neplanocin (**2**),[3] have been isolated from natural sources, the great majority of such analogues have been produced through laboratory syntheses. The synthesis of carbocylic ribonucleoside analogues has been motivated by an urgent need for antiviral agents and continues to be an especially active subdiscipline within this general area.[4]

Carbocylic ribose and deoxyribose analogues have been prepared by several methods in racemic form and, more rarely, in optically pure form. An important early example was the prep-

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