pyrones **7a**,[49] **7b**,[11a,21] **7h**,[21] **9a**,[28] **9b**,[27b] and **11**[50] have been previously reported. Spectral and analytical data for new compounds follow the general procedure.

To a deep green solution of 79 mg (0.104 mmol) of **5a** in 5 mL of toluene were successively added 0.21 mL (2.08 mmol) of benzaldehyde (a slight color change to olive green was observed) and 0.44 mL (2.3 mmol) of **6a**. After the reaction mixture was stirred for 15 h, 0.2 mL of TFA in 10 mL of $CCl_4$ was added and the solution was warmed to room temperature and evaporated under reduced pressure. The dark brown, oily residue was chromatographed on 50 g of silica gel with hexane/diethyl ether (3/2 v/v) as eluent.

**3-Acetoxy-6-phenyl-5,6-dihydro-4*H*-pyran-4-one (7c)**: $^1$H NMR ($CDCl_3$) $\delta$ 2.27 (s, 3 H), 2.66 (dd, $J$ = 3.5, 17, 1 H), 3.07 (dd, $J$ = 15, 17, 1 H), 5.54 (dd, $J$ = 3.5, 15, 1 H), 7.41 (m, 5 H), 7.50 (s, 1 H); MS $m/z$ 232 ($M^+$), 191, 190, 161, 144, 143, 104. Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.94; H, 5.66.

***cis*-3,5-Dimethyl-6-(2-furyl)-5,6-dihydro-4*H*-pyran-4-one (7d)**: $^1$H NMR ($CDCl_3$) $\delta$ 1.09 (d, $J$ = 6.5, 3 H), 1.70 (d, $J$ = 1, 3 H), 2.88 (dq, $J$ = 5, 7, 1 H), 5.45 (d, $J$ = 5, 1 H), 6.26 (m, 2 H), 7.20 (q, $J$ = 1, 1 H), 7.41 (m, 1 H); MS $m/z$ 192 ($M^+$), 174, 163, 136, 109, 108, 107. Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.73; H, 6.36.

***cis*-3,5-Dimethyl-6-(2-methoxyphenyl)-5,6-dihydro-4*H*-pyran-4-one (7e)**: $^1$H NMR ($CDCl_3$) $\delta$ 0.88 (d, $J$ = 7, 3 H), 1.74 (d, $J$ = 1, 3 H), 2.76 (dq, $J$ = 3, 7, 1 H), 3.80 (s, 3 H), 5.75 (d, $J$ = 3, 1 H), 6.88 (dd, $J$ = 8, 1, 1 H), 7.02 (td, $J$ = 8, 1, 1 H), 7.30 (m, 1 H), 7.39 (q, $J$ = 1, 1 H), 7.50 (m, 1 H). Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.64; H, 6.94.

***cis*-3,5-Dimethyl-6-(cyclohexyl)-5,6-dihydro-4*H*-pyran-4-one (7f)**: $^1$H NMR ($CDCl_3$) $\delta$ 0.78-1.00 (m, 2 H), 1.04 (d, $J$ = 7, 3 H), 1.05-1.37 (m, 3 H), 1.53-1.84 (m, 5 H), 1.66 (d, partially overlapping with previous m, $J$ = 1, 3 H), 2.14 (m, 1 H), 2.42 (dq, $J$ = 2, 7, 1 H), 3.88 (dd, $J$ = 2, 10, 1 H), 7.24 (q, $J$ = 1, 1 H); MS $m/z$ 208 ($M^+$), 190, 179, 165, 125, 124, 112, 95. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.67; H, 9.55.

***cis*-3,5-Dimethyl-6-(methoxycarbonyl)-5,6-dihydro-4*H*-pyran-4-one (7i)**: $^1$H NMR ($CDCl_3$) $\delta$ 1.13 (d, $J$ = 7, 3 H), 1.70 (d, $J$ = 1, 3 H), 2.84 (dq, $J$ = 3.5, 8, 1 H), 3.85 (s, 3 H), 4.95 (d, $J$ = 3.5, 1 H), 7.26 (q, $J$ = 1, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 10.5, 11.1, 41.9, 52.6, 79.5, 113.4, 157.0, 167.9, 195.0; MS $m/z$ 184 ($M^+$), 125, 101. Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.46; H, 6.64. Trans isomer: $^1$H NMR ($CDCl_3$) $\delta$ 1.23 (d, $J$ = 7, 3 H), 1.67 (d, $J$ = 1, 3 H), 2.88 (m, 1 H), 3.82 (s, 3 H), 4.66 (d, $J$ = 9, 1 H), 7.23 (q, $J$ = 1, 1 H).

**Pyrone 14a**: $^1$H NMR ($CDCl_3$) $\delta$ 1.13 (d, $J$ = 7, 3 H), 1.42 (s, 3 H), 1.46 (s, 3 H), 1.67 (d, $J$ = 1, 3 H), 2.30 (dq, $J$ = 3, 7, 1 H), 3.66 (dd, $J$ = 8, 8, 1 H), 4.10 (dd, $J$ = 6, 8, 1 H), 4.28 (dd, $J$ = 3, 8, 1 H), 4.43 (td, $J$ = 6, 8, 1 H), 7.29 (q, $J$ = 1, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 10.5, 10.6, 25.6, 26.5, 41.6, 65.2, 75.0, 82.7, 110.4, 112.6, 158.6, 196.2; MS $m/z$ 226 ($M^+$), 211, 169, 141, 126, 111, 101. Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.36; H, 7.84.

**Pyrone 14b**: $^1$H NMR ($CDCl_3$) $\delta$ 1.14 (d, $J$ = 8, 3 H), 1.45 (s, 3 H), 1.40 (s, 3 H), 1.66 (d, $J$ = 1, 3 H), 2.63 (dq, $J$ = 3, 8, 1 H), 4.01 (dd, $J$ = 4, 9, 1 H), 4.11-4.18 (m, 2 H), 4.28 (ddd, $J$ = 4, 6, 9, 1 H), 7.16 (q, $J$ = 1, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 10.2, 10.6, 25.1, 26.9, 40.9, 67.1, 72.9, 81.7, 109.8, 113.0, 157.9, 197.2. Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.99; H, 8.08.

**Pyrone 14c**: $^1$H NMR ($CDCl_3$) $\delta$ 1.26 (d, $J$ = 7, 3 H), 1.37 (s, 3 H), 1.44 (s, 3 H), 1.67 (d, $J$ = 1, 3 H), 2.56 (dq, $J$ = 7, 9, 1 H), 4.02 (dd, $J$ = 6, 9, 1 H), 4.06-4.15 (m, 2 H), 4.31 (q, $J$ = 6, 1 H), 7.17 (q, $J$ = 1, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 10.6, 12.4, 25.3, 26.4, 41.5, 66.1, 74.9, 83.3, 110.0, 112.8, 157.4, 194.6. Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.56; H, 7.99.

**Pyrone 14d**: $^1$H NMR ($CDCl_3$) $\delta$ 1.22 (d, $J$ = 8, 3 H), 1.38 (s, 3 H), 1.47 (s, 3 H), 1.67 (d, $J$ = 1, 3 H), 2.74 (dq, $J$ = 8, 12, 1 H), 3.96 (dd, $J$ = 3, 12, 1 H), 4.05 (dd, $J$ = 6, 8, 1 H), 4.09 (dd, $J$ = 6, 8, 1 H), 4.36 (td, $J$ = 3, 6, 1 H), 7.25 (q, $J$ = 1, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 10.5, 10.6, 25.3, 26.2, 40.9, 64.8, 74.3, 82.6, 109.9, 112.9, 158.1, 195.2. Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.30; H, 7.94.

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(49) Danishefsky, S.; Kerwin, J. F., Jr.; Kobayashi, S. *J. Am. Chem. Soc.* **1982**, *104*, 358.

(50) Danishefsky, S.; Harvey, D. F.; Quallich, G.; Uang, B. J. *J. Org. Chem.* **1984**, *49*, 393.

(51) Note Added in Proof: After the submission of this paper, we succeeded in growing crystals of complex **5a** suitable for X-ray diffraction. This was done by slow evaporation of a $CH_2Cl_2$ solution. **5a** was found to be *trimeric* in the solid state, with the oxo ligands in bridging positions and with a cis arrangement at each distorted-octahedral V(IV) center. According to Sloan (Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1) the observed absolute configuration at vanadium is [*OC*-6-33-Δ]. In contrast, **5a** was found to be *monomeric* in toluene or $CH_2Cl_2$ solution. Thus, the geometry of the complex in solution still remains unknown. The results of our structural studies will be reported at a later date.

# Intramolecular Cyclopropanation Reactions of Chromium (Alkenyloxy)carbene Complexes

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Chromium (aryl)(alkenyloxy)carbene complexes underwent intramolecular cyclopropanation reactions under mild conditions. Evidence for the intervention of metathesis/readdition and for "twist" addition followed by β-hydride elimination/reductive elimination was obtained. Carbenes of this class, sufficiently stable to isolate, underwent facile photochemical intramolecular cyclobutanone formation.

## Introduction

The thermal reaction of heteroatom-stabilized Fischer carbene complexes with electron-rich and electron-poor olefins to produce cyclopropanes was one of the earliest synthetically significant reactions of this class of complexes developed (eq 1).[1] The intermolecular version usually

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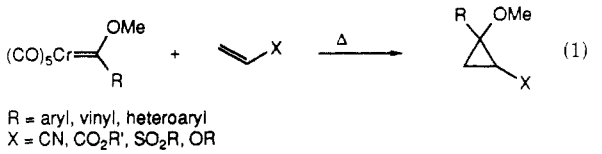
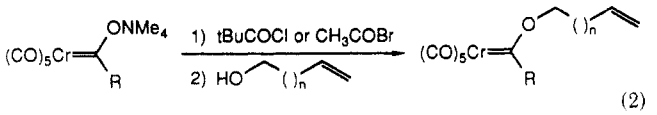



requires long reaction times at 80–100 °C and is limited to activated olefins. Simple alkenes such as styrenes do not react, and alkyl substitution on activated olefins reduces or prevents cyclopropanation. The intramolecular version, with a pendent olefin in either the alkyl group[2] or the alkoxy or amino group,[3] proceeds much more readily. Although this intramolecular process has been studied extensively from a mechanistic point of view, little attention has been given to the synthetic potential of this process.[4] In the course of developing intramolecular cyclobutanone formation by the photolysis of chromium (alkenyloxy)carbene complexes, it was observed in these laboratories that some (aryl)(alkenyloxy)carbenes were very unstable, undergoing intramolecular *cyclopropanation* reactions at temperatures as low as −20 °C.[5] To test the generality of these observations and to assess the synthetic potential of this process, the following studies were undertaken.

## Results and Discussion

The requisite chromium (alkenyloxy)carbene complexes were readily prepared by treating the tetramethylammonium acylate complex with pivaloyl chloride or acetyl bromide at −35 °C, followed by addition of the unsaturated alcohol and warming to room temperature (eq 2).[5] By this




procedure, a number of (alkenyloxy)carbene complexes were prepared and were subjected to thermolysis to produce cyclopropanated furans and pyrans in excellent yield (Table I).

The reactivity of some of these complexes was remarkable. Notwithstanding the fact that *inter*molecular cyclopropanation of simple alkenes by alkoxycarbene complexes occurs not at all[1] and that even activated olefins require elevated temperatures to undergo this same reaction, the corresponding intramolecular process with carbene complexes **1a–1d** proceeded at temperatures below 0 °C, even under CO pressure (90 psi), making these complexes impossible to isolate. Instead, fair to good yields of the cyclopropanated tetrahydrofurans **2a–2d** were isolated directly from the reaction mixture from complex preparation.[6] Carbene complexes **1c** and **1d**, having substituents $\alpha$ to the oxygen, cyclized to give single stereoisomers of the substituted tetrahydrofurans **2c** and **2d**, having the relative stereochemistry shown, as demonstrated by NOE measurements (see Experimental Section for details). This stereoselectivity is likely due to the difference in steric hindrance between the two possible metallacyclobutane precursors (Figure 1). The remainder of the carbene complexes studied were somewhat more robust.[7] They were easily isolated and purified, and the cyclopropanation reaction required heating to ensue at a reasonable rate, although, in one case (**1e**), a small amount of cyclopropane **2e** was isolated together with the carbene complex. Unsubstituted (complexes **1c**, **1d**, and **1g**), internal monosubstituted (**1a** and **1b**), terminal monosubstituted (**1h** and **1h'**), and terminal disubstituted (**1f**) olefins all underwent this process efficiently, while long-chain (alkenyloxy)carbene complexes (**1k**) were inert, slowly decomposing but producing no cyclopropanated product.

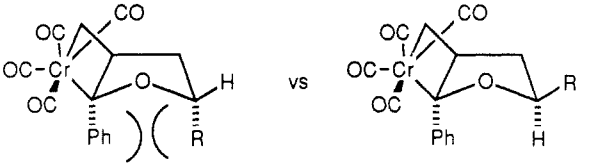



**Figure 1.**

*trans-* and *cis*-(hexenyloxy)carbenes **1h** and **1h'** offer some insight into the course of the reaction as well as into potential competing processes. Regardless of the initial geometry of the olefin, a mixture of endo (**2h'**) and exo (**2h**) products was obtained, along with traces of dihydrofuran **2h''**. The structures of **2h** and **2h'** were assigned by correlation of their respective $^1$H NMR spectra with the related cyclopropanes prepared herein and previously reported.[3a] For **2h**, the cyclopropyl proton $\alpha$ to the ethyl group ($\delta$ 1.39) couples to the other cyclopropyl proton with a small coupling constant ($J_{trans}$) of 5 Hz. For **2h'** ($\delta$ 1.53), the related coupling constant $J_{cis}$ is 9 Hz, supporting the assigned stereochemistry. The structure of **2h''** was confirmed by correlation with literature data.[8] These products are rationalized by the process shown in Scheme I and involves cycloaddition, followed by competitive reductive elimination to form cyclopropane, retaining stereochemistry of the olefin, metathesis with loss of dihydrofuran **2h''**, and metathesis/readdition/reductive elimination to give cyclopropane with inversion of olefin stereochemistry. This same process was proposed in a related tungsten

(1) For reviews on the cyclopropanation of olefins by chromium carbene complexes, see: (a) Casey, C. P. Metal-Carbene Complexes in Organic Synthesis. In *Transition Metals in Organic Synthesis, I*; Alper, H., Ed.; Academic Press: New York, 1976; pp 189–233. (b) Dötz, K. H. Carbene Complexes in Organic Synthesis. In *Transition Metal Carbene Complexes*; Seyferth, D., Ed.; Verlag Chemie: Weinheim, 1983, pp 192-226. (c) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (d) Reissig, H.-U. Donor-Acceptor Substituted Cyclopropanes via Fischer Carbene Complexes. In *Organometallics in Organic Synthesis*; Werner, H., Erker, G., Eds.; Springer-Verlag: Berlin, 1989; Vol. 2, p 311 and references therein.

(2) (a) Alvarez, C.; Levisalles, J.; Rudler, M.; Rudler, H.; Daran, J. C.; Jeannin Y. *J. Organomet. Chem.* **1982**, *228*, C7. (b) Alvarez, C.; Rudler, H.; Daran, J. C.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 574. (c) Alvarez, C.; Parlier, A.; Daran, J. C.; Rudler, H.; Rudler, M.; Knobler, C. *J. Organomet. Chem.* **1987**, *328*, 357.

(3) (a) Casey, C. P.; Shusterman, A. J. *Organometallics* **1985**, *4*, 736. (b) Casey, C. P.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 3754. (c) Casey, C. P.; Hornung, N. L.; Kosar, W. P. *J. Am. Chem. Soc.* **1987**, *109*, 4908.

(4) Reactions of alkynes with carbene complexes having remote olefins on the heteroatom side chain have been extensively studied, however: see: (a) Denise, B.; Goumount, R.; Parker, A.; Rudler, H.; Daran, J. C.; Vassermann, J. *J. Organomet. Chem.* **1989**, *377*, 89. (b) Rudler, H.; Parker, A.; Denise, B.; Yefsah, R.; Alvarez, C.; Daran, J. C.; Vassermann, J.; Knobler, C. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; NATO ASI Series C; Kluwer: Dordrecht, The Netherlands, 1989; Vol. 269; pp 279–292 and references therein. (c) Alvarez, C.; Parker, A.; Rudler, H.; Yefsah, R.; Daran, J. C.; Knobler, C. *Organometallics* **1989**, *8*, 2253.

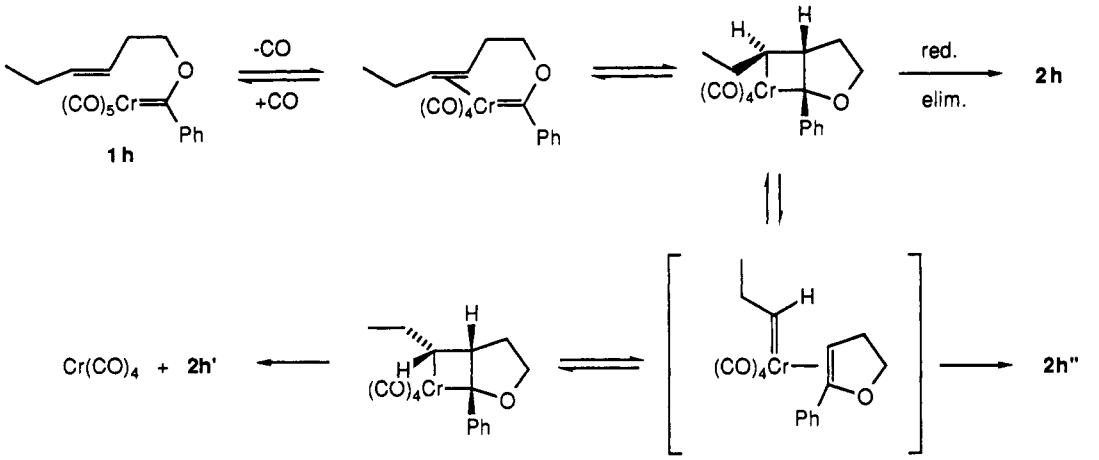
(5) Söderberg, B. C.; Hegedus, L. S.; Sierra, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 4364.

(6) Carbene complexes not stabilized by heteroatoms *do* cyclopropanate simple alkenes: (a) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282. (b) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. Closely related tungsten (alkenyloxy)carbene complexes were also quite reactive in this manner, undergoing intramolecular cyclopropanation in a few hours at 20–40 °C see ref 3a.

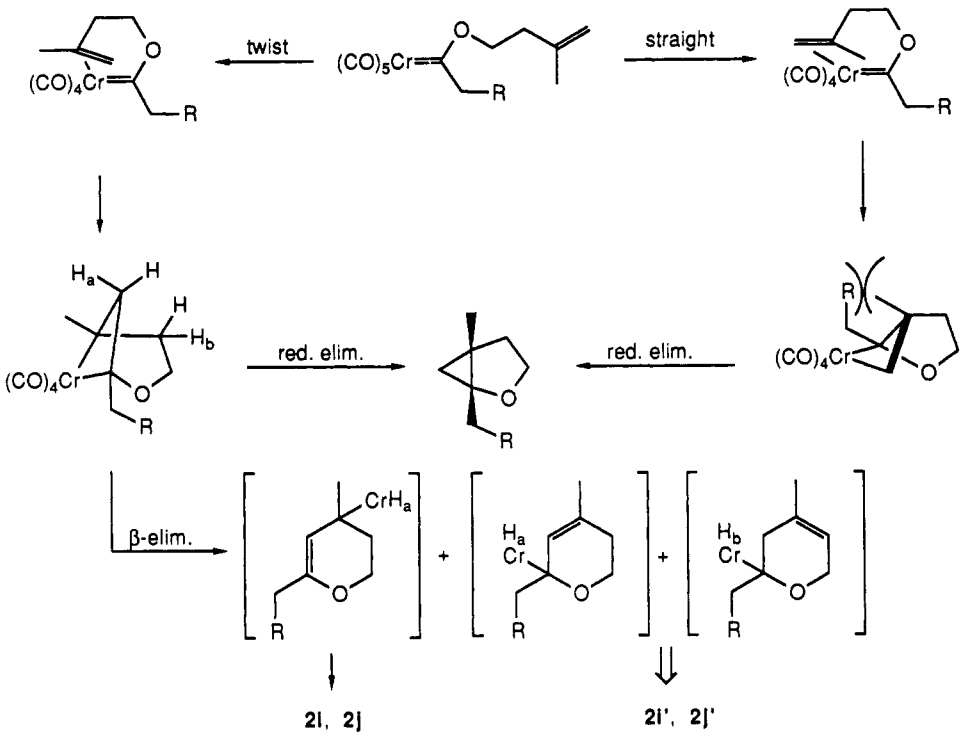
(7) The observed large differences in stability of the carbene complexes having very similar structures is striking and, at present, cannot be rationalized. The times and temperatures shown in Table I are those required for *complete* consumption of the carbene complex.

(8) Hercouet, A.; LeCorre, M. *Tetrahedron* **1981**, *37*, 2855.

**Scheme I**




**Scheme II**




carbene case for which the olefin was an enol ether [$(CO)_5W{=}C(OCH_2CH_2CH{=}CHOCH_3)(Ar)$].[3c] In this case, metathesis would produce an alkoxy-stabilized carbene complex ($W{=}CHOCH_3$), making this process energetically more favorable. It was stated that metathesis-type products were *not* observed with the related complex [$(CO)_5W{=}C(OCH_2CH_2CH{=}CH_2)(Ar)$] since an unstabilized carbene ($W{=}CH_2$) would have been produced. However, the results obtained with complexes **1h** and **1h'** indicate that metathesis can occur even when an unstabilized carbene fragment (Cr=CHEt) is produced.

The results obtained with complexes **1i** and **1j** reveal additional complexities. When the R group on the carbene carbon was changed from an aryl group to a benzyl or an alkyl group, the thermal reaction took a different course. With these complexes, the major products were isomeric alkylated dihydropyran derivatives **2i**, **2i'**, **2j**, and **2j'**, with cyclopropanated furans being *very* minor byproducts. These observations are best rationalized by the sequence shown in Scheme II. Metallacyclobutane formation can occur in two different regiochemical senses—straight or twist—which cannot be distinguished when cyclopropanation results, since both intermediates produce the same cyclopropane upon reductive elimination. However, the twist and straight metallacyclobutanes have different connectivities, and products **2i**, **2i'**, **2j**, and **2j'** can *only* result from the twist intermediate, by endocyclic β-elimination/reductive elimination. The twist mode of addition *may* have occurred with complexes **1i** and **1j** to minimize steric interactions between the carbene alkyl group and the methyl group on the olefin (Scheme II). It is less clear why β-elimination from the twist intermediate was more facile than reductive elimination. It is unlikely that the twist mode of addition was that followed for most of the cyclopropanations in Table I, since the isomerization and metathesis products from complexes **1h** and **1h'** could not have arisen from the twist intermediate.

Nitrogen-stabilized carbenes with a pendent olefin in the amino group also undergo thermal intramolecular cyclopropanation.[3] One case thereof is seen in Table I. Thus, thermolysis of **1l**, prepared in a similar way to the alkoxycarbenes, was readily converted into the cyclopropanated pyrrolidine deriv. **2l** in good yield.

Returning to the point that initiated these studies, those chromium (aryl)(alkenyloxy)carbenes that were stable enough to be isolated cleanly underwent the photochem-

**Table I. Intramolecular Cyclopropanation Reactions**

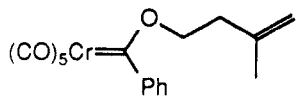
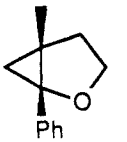
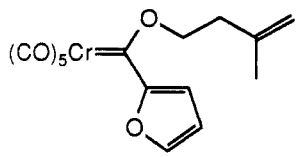
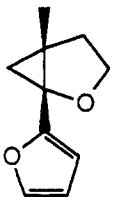
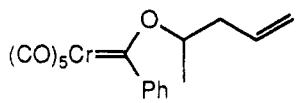
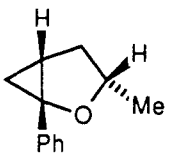
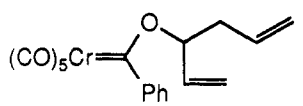
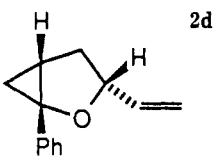
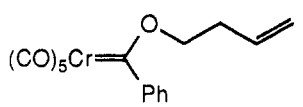
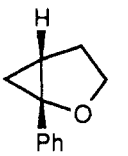
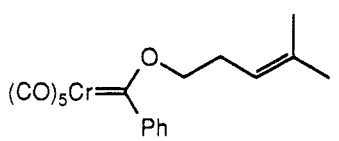
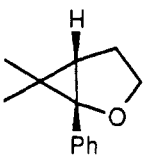
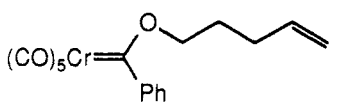
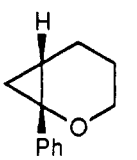
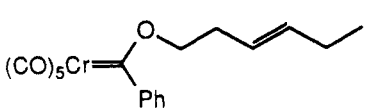
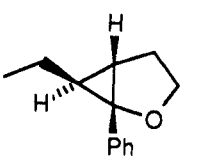
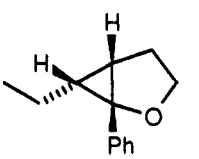
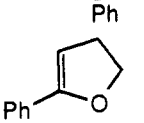
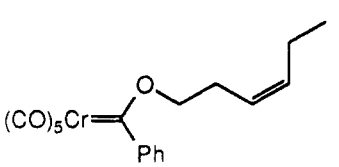
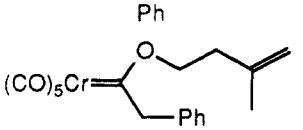
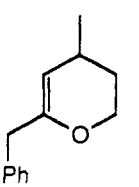
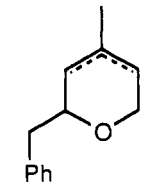
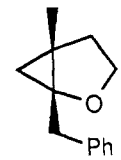
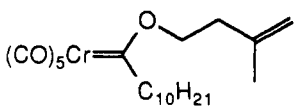
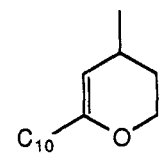
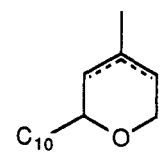
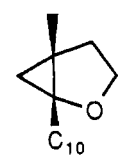
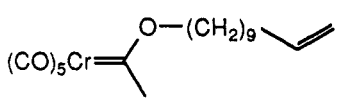
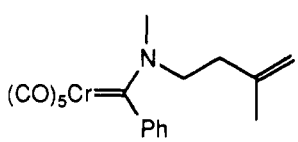
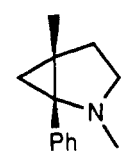
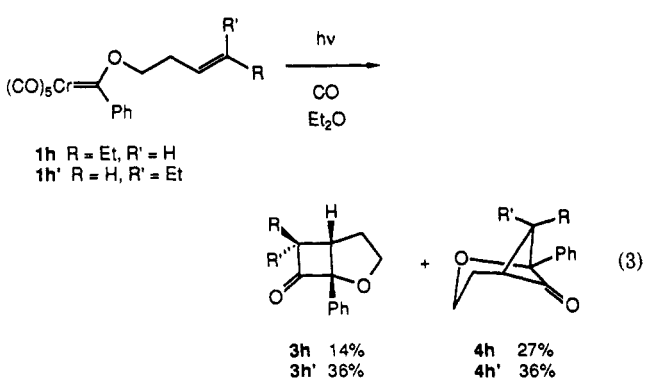
| carbene complex 1 | no. | yield, %[a] | thermolysis conditions | cyclopropane 2 | no. | yield, %[a] |
|---|---|---|---|---|---|---|
|  | **1a** | *b* | *b* |  | **2a** | 83 |
|  | **1b** | *b* | *b* |  | **2b** | 53 (19)[c] |
|  | **1c** | *b* | *b* |  | **2c** | 47 |
|  | **1d** | *b* | *b* |  | **2d** | 39 |
|  | **1e** | 60[d] | PhH/110 °C/2 h |  | **2e** | 88 |
|  | **1f** | 46 | PhH/118 °C/3.5 h |  | **2f** | 88 |
|  | **1g** | 66 | PhH/110 °C/17 h |  | **2g** | 92 |
|  | **1h** | 58 | PhH/90 °C/61 h; then 140 °C/25 h |  | **2h** | 52 |
| | | | |  | **2h′** | 20 |
| | | | |  | **2h″** | 4 |
|  | **1h′** | 61 | PhH/125 °C/53 h | | **2h**<br>**2h′** | 22<br>32 |
|  | **1i** | 26 | PhH/116 °C/18 h |  | **2i** | 33 |

**Table I** (Continued)

| carbene complex 1 | no. | yield, %[a] | thermolysis conditions | cyclopropane 2 | no. | yield, %[a] |
|---|---|---|---|---|---|---|
| | | | |  | 2i′ | 41 |
| | | | |  | 2i″ | 7 |
|  | 1j | 55 | PhH/120 °C/21 h |  | 2j | 30 |
| | | | |  | 2j′ | 48 |
| | | | |  | 2j″ | ~5 |
|  | 1k | | PhH/144 °C/87 h | | 1k | 44 |
|  | 1l | 95 | PhH/140 °C/21 h |  | 2l | 61 |

[a] Reported yields are for isolated, purified materials. [b] These complexes could not be isolated. They spontaneously decomposed to cyclopropanes **2** upon warming to room temperature during formation. [c] Direct mild thermolysis of the carbene-forming reaction gave an isolated yield of 19%. Short path silica gel column chromatography of the crude carbene-forming mixture followed. [d] 13% **2e** was also isolated.

ically driven intramolecular cyclobutanone formation previously developed (eq 3).[5] Thus, photolysis of **1h** and



**1h** R = Et, R′ = H
**1h′** R = H, R′ = Et

(3)

**3h** 14% **3h′** 36% **4h** 27% **4h′** 36%

**1h′** gave the expected products **3h** (14%) and **4h** (27%) and **3h′** and **4h′** (72%, 1:1 mixture) respectively. The regio- and stereochemistries were assigned by comparison with related compounds previously prepared.[5,9] The $^{13}C$ NMR spectra of the four compounds clearly distinguished the [3.1.1] system from the [3.2.0] system by the chemical shift of the CO resonance. In the case of **3h** and **3h′**, the CO is seen at lower field ($\delta$ 212.76 and 214.55) compared to the case of **4h** and **4h′** ($\delta$ 206.65 and 205.81) typical for a [3.2.0] and [3.1.1] system, respectively. The stereochemistry is based on homonuclear coupling constants ($^1H$ NMR), specifically, the vicinal couplings of the cyclobutanone protons. In the bicyclo[3.2.0] compounds (**3h** and **3h′**) $J_{cis}$ is larger than $J_{trans}$ (8.2 with respect to 5.2 Hz) as is expected for cyclobutanones. The stereochemistry of the isomeric bicyclo[3.1.1] compounds (**4h** and **4h′**) is deduced from the vicinal $J_{5,7}$ coupling of 5.7 Hz in the case of *endo*-**4h′** and 0 Hz in the case of *exo*-**4h**, clearly indicative of the proposed structures.

## Experimental Section

**General Procedure.** A Bruker ACS-300 NMR spectrometer was used for the 300-MHz $^1H$ NMR spectra and the 75-MHz $^{13}C$ NMR spectra. NMR spectra were recorded in $CDCl_3$, and the chemical shifts are given in parts per million (ppm) relative to $Me_4Si$ (0 ppm, $^1H$ and $^{13}C$), $CHCl_3$ (7.26 ppm, $^1H$), or $CDCl_3$ (77 ppm, $^{13}C$). Assignment of the $^{13}C$ spectra (broad band) is based on comparison in the measured substance class. $^1H$–$^1H$ coupling

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

constants are reported as calculated from spectra; thus, a slight difference between $J_{a,b}$ and $J_{b,a}$ is usually obtained. IR spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer. Chemical ionization (CI) mass spectra were obtained V. G. Micromass Ltd. Model 16F spectrometer.

For the purification of crude reaction mixtures, radial-layer (Chromatotron Model 7924) and column chromatographic techniques were applied in pentacarbonyl[(methyl)(10-undecen-1-yloxy)carbene]chromium(0) (**1k**),[5] 1-amino-3-methyl-3-butene,[12] Merck silica gel 60PF (for radial-layer chromatography) and Merck silica gel (230–400 mesh, 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: pentacarbonyl[tetramethylammonium (phenyl)carbenyl oxide]chromium(0),[10] pentacarbonyl[tetramethylammonium (furyl)carbenyl oxide]chromium(0),[11] pentacarbonyl[(benzyl)(3-methyl-3-buten-1-yloxy)carbene]chromium(0) (**1i**),[5] pentacarbonyl[(methyl)(10-undecen-1-yloxy)carbene]chromium(0) (**1k**),[5] 1-amino-3-methyl-3-butene,[12] 5-methyl-2-oxa-1-phenylbicyclo[3.1.0]hexane (**2a**).[5]

All other chemicals used herein were obtained from commercial sources or prepared as described below.

**General Procedure for the Preparation of the Chromium Carbenes 1e–l.** In an oven-dried 100-mL Airless flask equipped with a stir bar, 3 mmol of pentacarbonyl[tetramethylammonium (alkyl)carbenyl oxide]chromium(0) was dissolved in 75 mL of $CH_2Cl_2$. The solution was put under an argon atmosphere and cooled to −40 °C with an acetone–dry ice bath (some precipitation was observed). To the solution was added 3 mmol of either pivaloyl chloride or acetyl bromide by syringe. The reaction mixture was stirred for 1 h, allowing the temperature to go from −40 to −30 °C (the color changed to deep brown–red), after which the solution was recooled to −40 °C and 3 mmol of alcohol dissolved in 6 mL of $CH_2Cl_2$ was added by syringe. The temperature was allowed to slowly reach room temperature whereupon the color slowly changed to orange. To the 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 16 × 2 cm column, filled with silica gel, and purified by flash chromatography. A bright orange–red band was collected followed by solvent removal on 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[(3-buten-1-yloxy)(phenyl)carbene]chromium(0) (1e).** Reaction of 1.11 g (3.0 mmol) of pentacarbonyl[tetramethylammonium (phenyl)carbenyl oxide]chromium(0) in 50 mL of $CH_2Cl_2$ first with 370 μL (3.0 mmol) of pivaloyl chloride and then with 0.22 g (3.0 mmol) of 3-buten-1-ol in 6 mL of $CH_2Cl_2$ followed by slow warming (15 h) to room temperature gave after chromatography (hexane followed by hexane:$Et_2O$, 95:5) 0.63 g (1.79 mmol, 60%) of **1e** as an orange oil, followed by 0.06 g (0.38 mmol, 13%) of **2e** as a colorless oil. The product slowly decomposes to **2e** at 20 °C. $^1H$ NMR (broad signals) δ 7.2 (m, 5 H, ArH), 5.92 (m, 1 H, H3), 5.25 (m, 2 H, H4), 4.89 (s, 2 H, H1), 2.78 (q, 2H, $J$ = 6.2 Hz, H2); $^{13}C$ NMR δ 349.37 (Cr=C), 224.27 (*trans*-CO), 216.02 (4 C, *cis*-CO), 153.52 ($C_{ipso}$), 132.82, 130.09, 128.15, 122.76, 118.51, 79.73 (C1), 33.80 (C2); IR (film) ν 2062 (*trans*-CO), 1940 (*cis*-CO) $cm^{-1}$.

**Pentacarbonyl[(4-methyl-3-penten-1-yloxy)(phenyl)carbene]chromium(0) (1f).** Reaction of 1.11 g (3.0 mmol) of pentacarbonyl[tetramethylammonium (phenyl)carbenyl oxide]chromium(0) in 75 mL of $CH_2Cl_2$ first with 370 μL (3.0 mmol) of pivaloyl chloride and then with 0.30 g (3.0 mmol) of 4-methyl-3-penten-1-ol in 6 mL of $CH_2Cl_2$ gave, after slow warming to room temperature (5 h) followed by additional stirring for 3 h, after chromatography (hexane) 0.53 g (1.39 mmol, 46%) of **1f** as an orange oil. $^1H$ NMR (broad signals) δ 7.37 (s, 5 H, ArH), 5.19 (s, 1 H, H3), 4.78 (s, 2 H, H1), 2.69 (s, 2 H, H2), 1.72 (s, 3 H, Me), 1.67 (s, 3 H, Me); $^{13}C$ NMR δ 349.11 (Cr=C), 224.35 (*trans*-CO), 216.22 (4 C, *cis*-CO), 153.59 ($C_{ipso}$), 135.96 (C4), 129.94, 128.14, 122.59, 118.17, 80.51 (C1), 28.57, 25.74, 17.85: IR (film) ν 2061 (*trans*-CO), 1926 (*cis*-CO) $cm^{-1}$; MS (CI, $NH_3$) $m/e$ 206 ($M - Cr(CO)_5 + NH_4^+$), 189 ($M - Cr(CO)_5 + H^+$).

**Pentacarbonyl[(4-hexen-1-yloxy)(phenyl)carbene]chromium(0) (1g).** Reaction of 1.11 g (3.0 mmol) of pentacarbonyl[tetramethylammonium (phenyl)carbenyl oxide]chromium(0) in 75 mL of $CH_2Cl_2$ sequentially with 370 μL (3.0 mmol) of pivaloyl chloride and 0.26 g (3.0 mmol) of 4-hexen-1-ol in 6 mL of $CH_2Cl_2$ followed by slow warming (4 h) to room temperature gave after chromatography (hexane) 0.73 g (1.98 mmol, 66%) of **1g** as an orange oil. $^1H$ NMR (broad signals) δ 7.41 (s, 3 H, ArH), 7.25 (s, 2 H, ArH), 5.85 (s, 1 H, H4), 5.11 (s, 2 H, H5), 4.82 (s, 2 H, H1), 2.34 (s, 2 H), 2.13 (s, 2 H); $^{13}C$ NMR δ 349.57 (Cr=C), 224.29 (*trans*-CO), 216.17 (4 C, *cis*-CO), 153.62 ($C_{ipso}$), 136.58, 129.90, 128.15, 122.37, 116.15, 80.13 (C1), 29.88, 28.55; IR (film) ν 2061 (*trans*-CO), 1928 (*cis*-CO) $cm^{-1}$; MS (CI, $NH_3$) $m/e$ 192 ($M - Cr(CO)_5 + NH_4^+$), 174 ($M^+ - Cr(CO)_5$).

**Pentacarbonyl[(*trans*-3-hexen-1-yloxy)(phenyl)carbene]chromium(0) (1h).** Reaction of 371 mg (1.0 mmol) of pentacarbonyl[tetramethylammonium (phenyl)carbenyl oxide]chromium(0) in 25 mL of $CH_2Cl_2$ first with 135 μL (1.1 mmol) of pivaloyl chloride and then with 110 mg (1.1 mmol) of *trans*-3-hexen-1-ol in 4 mL of $CH_2Cl_2$ followed by slow warming (3 h, −40 to −10 °C, then 2 h at room temperature) gave, after chromatography (hexane), 220 mg (0.58 mmol, 58%) of **1h** as an orange oil. $^1H$ NMR (broad signals) δ 7.38 (s, 3 H, ArH), 7.24 (s, 2 H, ArH), 5.67 (s, 1 H, HC=C), 5.48 (s, 1 H, HC=C), 4.82 (s, 2 H, H1), 2.68 (s, 2 H, H2), 2.06 (s, 2 H, H5), 0.99 (s, 3 H, H6); $^{13}C$ NMR δ 349.06 (Cr=C), 224.32 (*trans*-CO), 216.23 (4 C, *cis*-CO), 153.53 ($C_{ipso}$), 136.49, 130.01, 128.14, 122.96, 122.72, 80.47 (C1), 32.83 (C2), 25.62 (C5), 13.54 (C6); IR (film) ν 2062 (*trans*-CO), 1933 (*cis*-CO) $cm^{-1}$; MS (CI, $NH_3$) $m/e$ 206 ($M - Cr(CO)_5 + NH_4^+$), 189 ($M - Cr(CO)_5 + H^+$).

**Pentacarbonyl[(*cis*-3-hexen-1-yloxy)(phenyl)carbene]chromium(0) (1h′).** Reaction of 1.11 g (3.0 mmol) of pentacarbonyl[tetramethylammonium (phenyl)carbenyl oxide]chromium(0) in 75 mL of $CH_2Cl_2$ sequentially with 405 μL (3.3 mmol) of pivaloyl chloride and 0.33 g (3.3 mmol) of *cis*-3-hexen-1-ol in 6 mL of $CH_2Cl_2$ followed by slow warming (4.5 h, −30 to −5 °C, then 2 h at room temperature) gave, after chromatography (hexane), 0.69 g (1.83 mmol, 61%) of **1h′** as an orange oil. $^1H$ NMR (broad signals) δ 7.34 (s, 5 H, ArH), 5.57 (s, 1 H, HC=C), 5.43 (s, 1 H, HC=C), 4.82 (s, 2 H, H1), 2.73 (s, 2 H, H2), 2.09 (s, 2 H, H5), 0.97 (s, 3 H, H6); $^{13}C$ NMR δ 349.13 (Cr=C), 224.26 (*trans*-CO), 216.18 (4 C, *cis*-CO), 153.60 ($C_{ipso}$), 135.60, 130.03, 128.08, 122.78, 122.56, 80.29 (C1), 27.58 (C2), 20.66 (C5), 14.00 (C6); IR (film) ν 2062 (*trans*-CO), 1928 (*cis*-CO) $cm^{-1}$; MS (CI, $NH_3$) $m/e$ 206 ($M - Cr(CO)_5 + NH_4^+$), 189 ($M - Cr(CO)_5 + H^+$).

**Pentacarbonyl[tetramethylammonium (*n*-decyl)carbenyl oxide]chromium(0).** In a 500-mL oven-dried Airless flask equipped with a stirbar was placed 6.16 g (28.0 mmol) of $Cr(CO)_6$ and 300 mL of $Et_2O$ (freshly distilled from benzophenone ketyl). The slurry was put under an argon atmosphere and cooled to 0 °C with an ice–$H_2O$ bath. To the slurry was added, by cannula, 44 mL (0.67 M, 29 mmol) of decyllithium as a $Et_2O$ solution over a 15-min period. Stirring was continued for 1 h at 0 °C followed by 4.5 h at room temperature. Solvent removal at reduced pressure (water aspirator) gave a brown solid residue. To the residue was added 50 mL of $H_2O$ followed by 12.3 g (84.0 mmol) of $BrNMe_4$(s) under vigorous stirring. After 10 min, the mixture was extracted with three 75-mL portions of $CH_2Cl_2$, the combined organic phase was dried ($MgSO_4$), and the solvent was removed on a rotary evaporator at reduced pressure to give a yellow oil with some black particles. The crude product was triturated with hexane (50 mL) and put on a 2-cm Celite pad. The pad was washed with hexane until a yellow band just began to elute. The band was eluted with $CH_2Cl_2$, and the solvent was removed to give 10.74 g (24.7 mmol, 85%) of the title compound as a viscous yellow oil. The product was contaminated with eicosane from coupling of decyllithium. The oil slowly solidifed at −20 °C, but even at this temperature a slow decomposition of product was observed. $^1H$ NMR (broad signals) δ 3.40 (s, 12 H, $NMe_4$), 2.76

(10) Fischer, E. O.; Aumann, R. *Chem. Ber.* **1968**, *101*, 960.
(11) Connor, J. A.; Jones, E. M. *J. Chem. Soc. A* **1971**, 1974.
(12) Prepared by the general method of: Mitsunobo, O.; Wada, H.; Sanot, T. *J. Am. Chem. Soc.* **1972**, *94*, 679. Previously prepared by: Levchenko, E. S.; Balón, J. G.: Kirsanov, A. *Zh. Org. Khim.* **1967**, *3*, 1883.

(s, 2 H, Cr=$CCH_2$), 1.24 (s, 16 H), 0.87 (s, 3 H, Me); $^{13}$C NMR δ 299.16 (Cr=C), 228.87 (*trans*-CO), 223.64 (4 C, *cis*-CO), 66.82, 56.48, 31.81, 29.69, 29.61, 29.56, 29.47, 29.26, 24.16, 22.57, 14.02; IR (film) ν 2029 (*trans*-CO), 1883 (*cis*-CO) cm$^{-1}$; MS (CI, $NH_3$) *m/e* 327 ($M^+$ - 4CO).

**Pentacarbonyl[(*n*-decyl)(3-methyl-3-buten-1-yloxy)carbene]chromium(0) (1j).** Reaction of a solution of 4.35 g (10.0 mmol) of pentacarbonyl[tetramethylammonium (*n*-decyl)carbenyl oxide]chromium(0) in 75 mL of $CH_2Cl_2$ first with 770 μL (10.0 mmol) of acetyl bromide (-40 °C, 20 min) followed by 0.86 g (10.0 mmol) of 3-methyl-3-buten-1-ol (16 h, -40 °C to room temperature) gave, after chromatography (hexane), 2.36 g (5.5 mmol, 55%) of **1j** as an orange oil that solidified when stored in a freezer. The product was still contaminated with eicosane that could not be removed, and it slowly decomposed even at -20 °C. $^1$H NMR (broad peaks) δ 5.08 (s, 2 H, $OCH_2$), 4.91 (s, 1 H, C=CH), 4.83 (s, 1 H, C=CH), 3.28 (s, 2 H, $OCH_2CH_2$), 2.69 (s, 2 H, Cr=$CCH_2$), 1.83 (s, 3 H, $CCH_3$=$CH_2$), 1.26 (s, 16 H), 0.88 (s, 3 H, $CH_3$); $^{13}$C NMR δ 361.24 (Cr=C), 223.20 (*trans*-CO), 216.50 (4 C, *cis*-CO), 140.47 ($CCH_2$=$CH_2$), 113.24 (C=$CH_2$), 79.65 ($OCH_2$), 63.25 (Cr=$CCH_2$), 37.24, 31.88, 29.53, 29.39, 29.30, 26.37, 22.68, 22.43, 14.08; IR (film) ν 2061 (*trans*-CO), 1929 (*cis*-CO) cm$^{-1}$; MS (CI, $NH_3$) *m/e* 256 (M - $Cr(CO)_5$ + $NH_4^+$), 239 (M - $Cr(CO)_5$ + $H^+$).

**Pentacarbonyl[(3-methyl-3-buten-1-ylamino)(phenyl)carbene]chromium(0).** A solution of 2.23 g (6.0 mmol) of pentacarbonyl[tetramethylammonium(phenyl)carbenyl oxide]chromium(0) in 75 mL of $CH_2Cl_2$ was treated first with 465 μL (6.0 mmol) of acetyl bromide (20 min, -40 °C) and then 1.02 g (20.0 mmol) of 1-amino-3-methyl-3-butene (18 h, -40 °C to room temperature) in 6 mL of $CH_2Cl_2$ to give, after chromatography (hexane:$Et_2O$, 95:5) 2.00 g (5.5 mmol, 91%) of the title compound as a pale orange-yellow oil. Spectral data are given for an inseparable 3:1 mixture of rotamers. Major isomer: $^1$H NMR (broad peaks) δ 9.03 (s, 1 H, NH), 7.39 (m, 3 H, ArH), 6.81 (m, 2 H, ArH), 5.00 (s, 1 H, H4), 4.89 (s, 1 H, H4), 3.26 (s, 2 H, H1), 2.27 (s, 2 H, H2), 1.69 (s, 3 H, $CH_3$); $^{13}$C NMR δ 281.78 (Cr=C), 223.41 (*trans*-CO), 217.16 (4 C, *cis*-CO), 149.63 ($C_{ipso}$), 140.31 (C4), 128.48, 126.75, 119.02, 114.70, 47.99 (C1), 37.35 (C2), 21.58 ($CH_3$). Minor isomer: $^1$H NMR (broad peaks) δ 8.51 (s, 1 H, NH), 7.21 (m, 3 H, ArH), 6.97 (m, 2 H, ArH), 4.93 (s, 1 H, H4), 4.84 (s, 1 H, H4), 4.19 (s, 2 H, H1), 2.55 (s, 2 H, H2), 1.82 (s, 3 H, $CH_3$); $^{13}$C NMR δ 278.70 (Cr=C), 223.77 (*trans*-CO), 217.25 (4C, *cis*-CO), 155.03 ($C_{ipso}$), 140.89 (C4), 128.57, 127.78, 121.03, 113.97, 50.45 (C1), 36.97 (C2), 21.85 ($CH_3$). Isomer mixture: IR (film) ν 2055 (*trans*-CO), 1914 (*cis*-CO) cm$^{-1}$; MS (CI, $NH_3$) *m/e* 310 (M - 2CO + $H^+$), 242 ($M^+$ - 5CO + $NH_3$), 174 (M - $Cr(CO)_5$ + $H^+$).

**Pentacarbonyl[(*N*-(3-methyl-3-buten-1-yl)-*N*-methylamino)(phenyl)carbene]chromium(0) (1l).** To a slurry of 5.5 mmol of hexane-washed (3 × 5 mL) NaH in 20 mL of freshly distilled THF (from benzophenone ketyl) was added, by syringe, a solution of 1.83 g (5.0 mmol) of pentacarbonyl[(3-methyl-3-buten-1-ylamino)(phenyl)carbene]chromium(0) in 50 mL of THF. After 20 min, 405 μL (6.5 mmol) of MeI dissolved in 30 mL of THF was added by syringe followed by stirring for 5 h. The solvent was removed on a rotary evaporator at water aspirator pressure. The crude oil obtained was chromatographed on a 11 × 2 cm column, eluting with hexane:$Et_2O$ (9:1) to afford after solvent removal 1.81 g (4.77 mmol, 96%) of **1l** as a yellow oil. Spectral data are given for an inseparable ca. 3:1 mixture of rotamers. Major isomer: $^1$H NMR δ 7.37 (m, 2 H, ArH), 7.14 (m, 1 H, ArH), 6.70 (m, 2 H, ArH), 4.73 (t, 1 H, *J* = 1.5 Hz, H4), 4.56 (s, 1 H, H4), 3.96 (s, 3 H, NMe), 3.44 (m, A of an $A_2X_2$, 2 H, H1), 2.25 (apparent t, X of an $A_2X_2$, 2 H, H3), 1.46 (s, 3 H, Me—C3); $^{13}$C NMR δ 276.21 (Cr=C), 224.00 (*trans*-CO), 217.26 (4 C, *cis*-CO), 152.09 ($C_{ipso}$), 140.45 (C3), 128.30 (2 C), 125.73, 119.08 (2 C), 113.19, 57.03 (NMe), 48.95 (C1), 36.75 (C2), 22.02 (Me—C3). Minor isomer: $^1$H NMR δ 7.37 (m, 2 H, ArH), 7.14 (m, 1 H, ArH), 6.70 (m, 2 H, ArH), 4.94 (s, 1 H, H4), 4.88 (s, 1 H, H4), 4.42 (m, A of an $A_2X_2$, 2 H, H1), 3.01 (s, 3 H, NMe), 2.63 (m, X of an $A_2X_2$, H2), 1.87 (s, 3 H, Me—C3); $^{13}$C NMR δ 274.71 (Cr=C), 223.84 (*trans*-CO), 217.16 (4 C, *cis*-CO), 153.39 ($C_{ipso}$), 141.06 (C3), 128.69 (2 C), 126.75, 118.50 (2 C), 112.68, 62.20 (NMe), 43.52 (C1), 36.07 (C2), 22.60 (Me—C3). Both isomers: IR (film) ν 2053 (*trans*-CO), 1915 (*cis*-CO) cm$^{-1}$; MS (CI, $NH_3$) *m/e* 187 ($M^+$ - $Cr(CO)_5$).

**1-(1-Furyl)-5-methyl-2-oxabicyclo[3.1.0]hexane (2b).** Reaction of 2.78 g (7.7 mmol) of pentacarbonyl[tetramethylammonium (1-furyl)carbenyl oxide]chromium(0) in 100 mL of $CH_2Cl_2$ first with 685 μL (9.23 mmol) of acetyl bromide (30 min, -35 °C) and then with a solution of 0.80 g (9.23 mmol) of 3-methyl-3-buten-1-ol in 6 mL of $CH_2Cl_2$ (15 h, -35 °C to room temperature followed by 8 h at room temperature) gave, after chromatography (petroleum ether:$Et_2O$, 9:1), 0.85 g of a deep red semisolid. A second chromatography afford 177 mg (0.66 mmol, 9%) of pentacarbonyl[(1-furyl)(3-methyl-3-buten-1-yloxy)carbene]chromium(0) as an orange-yellow oil. The oil was immediately dissolved in 20 mL of $Et_2O$ in a 40-mL Fischer & Porter pressure tube. 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. After 24 h, the solvent was removed from the colorless solution and the residue was flash chromatographed on a 5 × 2 cm column, eluting with hexane:$Et_2O$ (9:1). The solvents were removed on a rotary evaporator at water aspirator pressure to afford 57 mg (0.35 mmol, 57%, 5% from the ammonium salt) of **2b** as a pale yellow oil. The product slowly decomposes at room temperature, thus making an elemental analysis impossible. $^1$H NMR δ 7.39 (m, 1 H, furyl), 6.34 (m, 1 H, furyl), 6.30 (m, 1 H, furyl), 4.14 (ddd, 1 H, $J_{3,3'}$ = 9.2, $J_{3,4}$ = 7.5, $J_{3,4'}$ = 3.9 Hz, H3), 3.57 (q, 1 H, $J_{3',3} = J_{3',4} = J_{3',4'}$ = 9.0 Hz, H3'), 2.11 (m, 2 H, H4 and H4'), 1.38 (d, 1 H, $J_{6,6'}$ = 6.4 Hz, H6), 1.13 (s, 3 H, Me), 0.94 (d, 1 H, $J_{6',6}$ = 6.4 Hz, H6'); $^{13}$C NMR δ 151.80 (furyl-C1), 142.35 (furyl-C4), 110.12 (furyl), 108.12 (furyl), 67.31 (C1), 65.68 (C3), 35.20, 28.67 (C5), 19.19, 17.83; IR (film) ν 2949, 1160, 1127, 1099, 1068, 1042, 999, 736, 476, 474 cm$^{-1}$; MS (CI, $NH_3$) *m/e* 181 ($M^+$ + $NH_3$), 165 (M + $H^+$), 164 ($M^+$).

Similar treatment of 1.08 g (3.0 mmol) of pentacarbonyl[tetramethylammonium (1-furyl)carbenyl oxide]chromium(0) with acetyl bromide (225 μL, 3.0 mmol, -40 °C, 30 min) and 3-methyl-3-buten-1-ol (0.26 g, 3.0 mmol, room temperature 18 h, reflux 1.5 h) gave after solvent removal a brown residue. The residue was slurried up in 80 mL of hexane:$Et_2O$ (1:1) and air-oxidized for 22 h in a lightbox (6 × 20-W Vitalite fluorescent bulbs).[13] The colorless solution with a brown-green precipitate was filtered through a Celite pad (the pad was washed with 30 mL of $Et_2O$) followed by solvent removal. The crude semisolid was chromatographed on a 16 × 2 cm column, eluting with hexane:$Et_2O$ (9:1) to give 91 mg (0.55 mmol, 19%) of **2b** as a pale yellow oil.

***endo*-3-Methyl-2-oxa-1-phenylbicyclo[3.1.0]hexane (2c).** Reaction of 1.11 g (3.0 mol) of pentacarbonyl[tetramethylammonium (phenyl)carbenyl oxide]chromium(0) with 370 μL (3.0 mmol) of pivaloyl chloride (1 h, -40 to -25 °C) in 75 mL of $CH_2Cl_2$ followed by a solution of 0.26 g (3.0 mmol) of 3-methyl-3-buten-1-ol (18 h, room temperature) in 6 mL of $CH_2Cl_2$ afforded a green-yellow solution. The solvent was removed and the residue dissolved in 80 mL of hexane:$Et_2O$ (1:1) and air-oxidized in the lightbox for 24 h. A blue-green solution with some precipitate was formed. The solution was filtered (Celite), and the solvents were removed to give a blue-green oil that was chromatographed (hexane, 50 mL followed by hexane:$Et_2O$, 95:5) to give 295 mg of a pale blue oil. The oil was further purified by short path distillation (ca. 1 mmHg, 50-100 °C) to afford 244 mg (1.40 mmol, 47%) of **2c** as a colorless oil. $^1$H NMR δ 7.34-7.17 (m, 5 H, ArH), 4.73 (quintet d, 1 H, $J_{3,4}$ = 8.9, $J_{3,4'} = J_{3,Me}$ = 6.4 Hz, H3), 2.53 (td, 1 H, $J_{4',4}$ = 12.9, $J_{4',3} = J_{4',5}$ = 6.6 Hz, H4'), 1.83 (m, 1 H, H4), 1.55 (m, 2 H, H5 and H6), 1.27 (d, 3 H, $J_{Me,3}$ = 6.1 Hz, Me-C3), 1.15 (t, 1 H, $J_{6',6} = J_{6',5}$ = 5.4 Hz, H6'); $^{13}$C NMR δ 141.98 ($C_{ipso}$), 128.16 (2 C), 125.97, 123.91 (2 C), 84.24 (C3), 71.17 (C1), 39.58, 30.55, 29.02, 21.68; IR (film) ν 2970, 2920, 2865, 1498, 1449, 1197, 1083, 752, 697 cm$^{-1}$; MS (CI, $NH_3$) *m/e* 192 (M + $NH_4^+$), 175 (M + $H^+$). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.66; H, 8.10.

***endo*-2-Oxa-1-phenyl-3-vinylbicyclo[3.1.0]hexane (2d).** Reaction of 1.11 g (3.0 mmol) of pentacarbonyl[tetramethylammonium (phenyl)carbenyl oxide]chromium(0) with 370 μL (3.0 mmol) of pivaloyl chloride in 75 mL of $CH_2Cl_2$ followed by 0.29 g (3.0 mmol) of 1,5-hexadien-3-ol in 6 mL of $CH_2Cl_2$ as described for **2c** afforded a green-orange solution. The solvent was removed on a rotary evaporator, and the residue was chromatographed on

(13) To remove arene-bound chromium and simplify purification.

a 15 × 2 cm column, eluting with hexane:$Et_2O$ (95:5) to give 350 mg of an orange–red oil consisting mostly of **2d**. The oil was taken up in 80 mL of hexane:$Et_2O$ (1:1) and air-oxidized in a lightbox for 4 h.[13] The formed brown precipitate was filtered off through Celite, and the solvents were removed on a rotary evaporator. Chromatography (16 × 2 cm column, hexane:$Et_2O$, 95:5) gave 0.22 g (1.18 mmol, 39%) of **2d** as a colorless oil. $^1H$ NMR $\delta$ 7.35 (m, 4 H, Ar), 7.23 (m, 1 H, Ar), 5.89 (ddd, 1 H, $J_{trans}$, 17.1, $J_{cis}$ = 10.5, $J_{vic}$ = 6.5 Hz, C*H*=$CH_2$), 5.30 (td, 1 H, $J_{trans}$ = 17.2, $J_{gem}$ = $J_{allyl}$ = 1.4 Hz, CH=C$H_2$), 5.15 (td, 1 H, $J_{cis}$ = 10.4, $J_{gem}$ = $J_{allyl}$ = 1.4 Hz, CH=C$H_2$), 5.08 (apparent tq, $J$ = 7.7, 1.2 Hz, H3), 2.61 (m, 1 H, H5), 1.86 (m, 2 overlapping H, H4), 1.48 (ddd, 1 H, $J_{6,5}$ = 9.1, $J_{6,6'}$ = 5.8, $J_{6,4}$ = 1.0 Hz, H6), 1.27 (t, 1 H, $J_{6',6}$ = $J_{6',5}$ = 5.5 Hz, H6′); $^1H$ NOE irradiation at $\delta$ 1.27 gave a small NOE at $\delta$ 5.89; $^{13}C$ NMR $\delta$ 141.43 ($C_{ipso}$), 139.63 (*C*H=$CH_2$), 128.08 (2 C), 126.02, 123.97, (2 C), 115.46 (CH=$CH_2$), 87.06 (C3), 71.27 (C1), 37.40, 28.32, 27.91; IR (film) $\nu$ 3062, 3033, 2986, 2930, 2870, 1498, 1449, 1196, 926, 753, 696 $cm^{-1}$; MS (CI, $NH_3$) $m/e$ 204 (M + $NH_4^+$), 187 (M + $H^+$). Anal. Calcd for $C_{13}H_{14}O$: C, 83.80; H, 7.58. Found: C, 84.12; H, 7.62.

**General Procedure for the Thermolysis of the Chromium Carbenes 1e–l.** In an oven-dried 40-mL Fischer & Porter pressure tube equipped with a stir bar was prepared a ca.0.1 M solution of carbene in benzene. Argon was bubbled through the solution for 5 min to remove oxygen. The tube was capped, and the solution was heated to 110–145 °C, depending on the substrate, until all carbene had been consumed (2–53 h). The solvent was removed on a rotary evaporator at water aspirator pressure. The residue was dissolved in hexane:$Et_2O$ (1:1) and air-oxidized in a lightbox (see **2b**) until the solution was colorless.[13] The formed precipitate was removed by filtration (Celite), the filter was washed with $Et_2O$, and the solvents were removed at reduced pressure (rotary evaporator). The crude product was purified either by radial chromatography or flash chromatography.

**2-Oxa-1-phenylbicyclo[3.1.0]hexane (2e).** Thermolysis of 631 mg (1.79 mmol) of **1e** in 20 mL of benzene (110 °C, 2 h) followed by oxidation (22 h) gave a colorless oil together with some white precipitate. The crude product was purified by radial chromatography (2-mm plate) eluting with hexane:$Et_2O$ (96:4) to afford, after solvent removal, 251 mg (1.57 mmol, 88%) of **2e** as a colorless oil. $^1H$ NMR $\delta$ 7.30 (m, 4 H, Ar), 7.20 (m, 1 H, Ar), 4.21 (dt, 1 H, $J_{3,3'}$ = $J_{3,4}$ = 9.0; $J_{3,4'}$ = 2.7 Hz, H3), 3.71 (dt, 1 H, $J_{3',3}$ = $J_{3',4'}$ = 9.4, $J_{3',4}$ = 7.4 Hz, H3′), 2.23 (m, 1 H, H4), 2.02 (ddd, 1 H, $J_{4',4}$ = 11.9, $J_{4',3}$ = 7.4, $J_{4',3'}$ = 2.7 Hz, H4′), 1.72 (td, 1 H, $J_{5,6}$ = 9.5, $J_{5,4}$ = $J_{5,6'}$ = 4.9 Hz, H5), 1.33 (t, 1 H, $J_{6',6}$ = $J_{6',5}$ = 5.9 Hz, H6′), 1.12 (ddd, 1 H, $J_{6,5}$ = 9.0, $J_{6,6'}$ = 6.5, $J_{6,4}$ = 0.8 Hz, H6); $^{13}C$ NMR $\delta$ 140.81 ($C_{ipso}$), 128.26 (2 C), 126.23, 124.50 (2 C), 69.40 (C1), 67.17 (C3), 29.14, 25.28, 17.79; IR (film) $\nu$ 3061, 3034, 2947, 2873, 1451, 1097, 1063, 752, 697 $cm^{-1}$; MS (CI, $NH_3$) $m/e$ 178 (M + $NH_4^+$), 161 (M + $H^+$). Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.33; H, 7.41.

**6,6-Dimethyl-2-oxa-1-phenylbicyclo[3.1.0]hexane (2f).** Thermolysis of 365 mg (0.96 mmol) of **1f** in 20 mL of benzene (118 °C, 3.5 h) followed by oxidation (17 h) gave after filtration and solvent removal 159 mg (0.85 mmol, 88%) of pure **2f** as a colorless oil. $^1H$ NMR $\delta$ 7.42–7.21 (m, 5 H, ArH), 4.22 (q, 1 H, $J_{3,3'}$ = $J_{3,4}$ = $J_{3,4'}$ = 8.7 Hz, H3) 3.94 (dt, 1 H, $J_{3',3}$ = $J_{3',4'}$ = 8.6, $J_{3',4}$ = 3.6 Hz, H3′), 2.24 (dddd, 1 H, $J_{4,4'}$ = 12.6, $J_{4,3}$ = 8.8, $J_{4,5}$ = 7.3, $J_{4,3'}$ = 3.6 Hz, H4), 1.99 (dtd, 1 H, $J_{4',4}$ = 12.7, $J_{4',3}$ = $J_{4',3'}$ = 8.8, $J_{4',5}$ = 1.6 Hz, H4′), 1.69 (dd, 1 H, $J_{5,4}$ = 7.3, $J_{5,4'}$ = 1.6 Hz, H5), 1.21 (s, 3 H, Me), 0.82 (s, 3 H, Me); $^{13}C$ NMR $\delta$ 138.00 ($C_{ipso}$), 128.44 (2 C), 127.87 (2 C), 127.04, 78.16 (C1), 74.92 (C3), 31.52, 31.23 (C6), 26.65, 23.47, 14.61; IR (film) $\nu$ 2946, 1688, 1449, 1275, 785, 732, 699 $cm^{-1}$; MS (CI, $NH_3$) $m/e$ 206 (M + $NH_4^+$), 189 (M + $H^+$). Anal. Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.89; H, 8.47.

**2-Oxa-1-phenylbicyclo[4.1.0]heptane (2g).** Thermolysis of 726 mg (1.98 mmol) of **1g** in 20 mL of benzene (110 °C, 17 h) followed by oxidation (23 h) gave a pale yellow oil with some solid $Cr(CO)_6$ after filtration and solvent removal. The crude was purified by radial chromatography (2-mm plate), eluting first with 100 mL of hexane followed by hexane:$Et_2O$ (98:2) to give 316 mg (1.82 mmol, 92%) of **2g** as a colorless oil. $^1H$ NMR $\delta$ 7.23–7.03 (m, 5 H, Ar), 3.69 (td, 1 H, $J_{3,3'}$ = 10.7, $J_{3,4}$ = $J_{3,4'}$ = 3.2 Hz, H3), 3.30 (dt, 1 H, $J_{3',3}$ = $J_{3',4}$ = 10.5, $J_{3',4'}$ = 3.3 Hz, H3′) 1.88 (m, 2 H, H4), 1.42 (m, 2 H, H5), 1.27 (m, 1 H, H6), 1.09 (dd, 1 H, $J_{7,6}$ = 9.9, $J_{7,7'}$ = 5.2 Hz, H7), 1.01 (dd, 1 H, $J_{7',6}$ = 7.9, $J_{7',7}$ = 5.5 H, H7′); $^{13}C$ NMR $\delta$ 144.52 ($C_{ipso}$), 128.16 (2 C), 125.70, 123.43 (2 C), 64.57 (C3), 59.72 (C1), 22.51, 21.52 (2 C), 20.10; IR (film) $\nu$ 2931, 2856, 1603, 1493, 1454, 1374, 1278, 1234, 1131, 1062, 738, 697 $cm^{-1}$; MS (CI, $NH_3$) $m/e$ 192 (M + $NH_4^+$), 175 (M + $H^+$). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.92; H, 7.84.

***exo*-6-Ethyl-2-oxa-1-phenylbicyclo[3.1.0]hexane (2h), *endo*-6-Ethyl-2-oxa-1-phenylbicyclo[3.1.0]hexane (2h′), and 3,4-Dihydro-1-phenylfuran (2h″).** Thermolysis of 573 mg (1.51 mmol) of **1h** (90 °C, 61 h followed by 140 °C, 25 h) and air oxidation (24 h) gave after filtration and solvent removal 213 mg of a 13:5:1 mixture of **2h**:**2h′**:**2h″** (52%, 20%, 4%). The products were separated by flash chromatography (12 × 2 cm column, hexane:$Et_2O$, 9:1) to give pure **2h** and **2h′** both as colorless oils. Spectral data of **2h″** from the crude mixture was in complete accordance with literature values.[8] **2h**: $^1H$ NMR $\delta$ 7.40–7.22 (m, 5 H, Ar), 4.15 (dt, 1 H, $J_{3,3'}$ = $J_{3,4}$ = 8.9, $J_{3,4'}$ = 3.0 Hz, H3), 3.72 (dt, 1 H, $J_{3',3}$ = $J_{3',4}$ = 9.0, $J_{3',4'}$ = 7.5 Hz, H3′), 2.23 (dtd, 1 H, $J_{4,4'}$ = 11.9, $J_{4,3}$ = $J_{4,3'}$ = 9.1, $J_{4,5}$ = 5.3 Hz, H4), 2.05 (ddd, 1 H, $J_{4',4}$ = 11.9, $J_{4',3'}$ = 7.5, $J_{4',3}$ = 3.0 Hz, H4′), 1.63 (t, 1 H, $J_{5,4}$ = $J_{5,6}$ = 5.0 Hz, H5), 1.39 (dt, 1 H, $J_{6,CH_2}$ = 7.2 $J_{6,5}$ = 4.7 Hz, H6), 1.12 (sextet, 1 H, $J_{CH_2,Me}$ = $J_{CH_2,6}$ = 7.3 Hz, $CH_2$), 1.02 (sextet, $J_{CH_2,Me}$ = $J_{CH_2,6}$ = 7.2 Hz, $CH_2$), 1.02 (sextet, $J_{CH_2,Me}$ = $J_{CH_2,6}$ = 7.2 Hz, $CH_2$), 0.80 (t, 3 H, Me); $^{13}C$ NMR $\delta$ 136.80 ($C_{ipso}$), 128.16 (2 C), 127.91 (2 C), 127.22, 74.63 (C1), 67.79 (C3), 30.90, 29.35, 26.06, 21.78, 13.17 (Me); IR (film) $\nu$ 2958, 2872, 1448, 1072, 761, 699, 668 $cm^{-1}$; MS (CI, $NH_3$) $m/e$ 206 (M = $NH_4^+$), 189 (M + $H^+$). Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.92; H, 8.33.

**2h′**: $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.28 (m, 4 H, Ar), 7.18 (m, 1 H, Ar), 4.35 (q, 1 H, $J_{3,3'}$ = $J_{3,4}$ = $J_{3,4'}$ = 8.6 Hz, H3), 4.06 (dt, 1 H, $J_{3',3}$ = $J_{3',4'}$= 8.5, $J_{3',4}$ = 3.7 Hz, H3′) 2.25 (dtd, 1 H, $J_{4,4'}$ = 12.6, $J_{4,3}$ = $J_{4,5}$ = 8.8, $J_{4,3'}$ = 3.8 Hz, H4), 1.98 (dtd, 1 H, $J_{4',4}$ = 12.6, $J_{4',3}$ = $J_{4',3'}$ = 8.7, $J_{4',5}$ = 1.8 Hz, H4′), partly overlapping 1.91 (dt, 1 H, $J_{5,4}$ = $J_{5,6}$ = ca. 9, $J_{5,4'}$ = 1.7 Hz, H5), 1.53 (m, 3 H, H6 and $CH_2$), 1.04 (t, 3 H, $J$ = 7.2 Hz, Me); $^{13}C$ NMR $\delta$ 142.77 ($C_{ipso}$), 128.13 (2 C), 125.83, 123.88 (2 C), 76.06 (C3), 73.39 (C1), 37.57, 30.82, 26.12, 15.85, 13.85; IR (film) $\nu$ 2959, 2872, 1602, 1498, 1448, 1143, 1110, 1070, 749, 696 $cm^{-1}$; MS (CI, $NH_3$) $m/e$ 206 (M + $NH_4^+$), 189 (M + $H^+$). Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: 83.12: H, 8.40.

Thermolysis of 380 mg (1.00 mmol) of **1h′** in 20 mL of benzene (125 °C, 53 h) followed by air oxidation (37 h) gave after standard workup 60 mg (0.32 mmol, 32%) of **2h′** followed by 41 mg (0.22 mmol, 22%) of **2h** both as colorless oils.

**Thermolysis of 1i.** Thermolysis of 474 mg (1.25 mmol) of **1i** in 20 mL of benzene (116 °C, 8 h) followed by air oxidation (16 H) gave after radial chromatography (2-mm plate; hexane:$Et_2O$, 95:5; hexane:$Et_2O$, 9:1) 77 mg (0.41 mmol, 33%) of 2-benzyl-4,5-dihydro-4-methyl-6*H*-pyran (**2i**) followed by 114 mg (0.61 mmol, 48%) of a 66:19:15 mixture of isomeric **2i′** (see Table I) and 1-benzyl-5-methyl-2-oxabicyclo[3.1.0]hexane (**2i″**). **2i′** could be separated from **2i″** by radial chromatography (2-mm plate, hexane:$Et_2O$, 95:5). Although pure by $^1H$ NMR and $^{13}C$ NMR spectroscopies **2i** did not give satisfactory elemental analysis. **2i**: $^1H$ NMR $\delta$ 7.31–7.17 (m, 5 H, Ar), 4.43 (d, 1 H, $J_{3,4}$ = 2.8 Hz, H3), 4.40 (ddd, 1 H, $J_{6,6'}$ = 10.7, $J_{6,5}$ = 6.1, $J_{6,5'}$ = 3.4 Hz, H6), 3.90 (ddd, 1 H, $J_{6',6}$ = 10.7, $J_{6',5'}$ = 8.7, $J_{6',5}$ = 2.7 Hz, H6′), 3.29 (s, 2 H, Ar$CH_2$), 2.28 (m, 1 H, H4), 1.85 (ddtd, 1 H, $J_{5,5'}$ = 13.6, $J_{5,4}$ = $J_{5,6}$ = 6.2, $J_{5,6'}$ = 2.8, $J_{5,3}$ = 0.9 Hz, H5), 1.43 (dddd, $J_{5',5}$ = 13.5, $J_{5',4}$ = 10.8, $J_{5',6'}$ = 8.8, $J_{5',6}$ = 3.4 Hz, H5′), 0.98 (d, 3 H, $J_{Me,4}$ = 6.9 Hz, Me); $^{13}C$ NMR $\delta$ 152.52, 138.73, 128.76 (2 C), 128.21 (2 C), 126.14, 104.12 (C2), 64.87 (C6), 40.69 (Ar$CH_2$), 30.76 (C4), 25.81 (C5), 22.17 (Me); IR (film) $\nu$ 3028, 2955, 2869, 1670, 1154, 1081, 702 $cm^{-1}$; MS (CI, $NH_3$) $m/e$ 189 (M + $H^+$).

Major **2i′** was assigned as 2-benzyl-5,6-dihydro-4-methyl-1*H*-pyran and minor **2i′** as 2-benzyl-2,3-dihydro-4-methyl-6*H*-pyran. From a ca. 3:1 mixture, the following spectral data were obtained. Major isomer: $^1H$ NMR $\delta$ 7.33–7.17 (m, 5 H, Ar), 5.33 (m, 1 H, H3), 4.25 (m, 1 H, H2), 3.99 (ddd, 1 H, $J_{6,6'}$ = 11.3, $J_{6,5}$ = 5.7, $J_{6,5'}$ = 2.7 Hz, H6), 3.61 (ddd, 1 H, $J_{6,6'}$ = 11.3, $J_{6',5'}$ = 9.8, $J_{6',5}$ = 4.0 Hz, H6′), 2.90 (dd, 1 H, $J_{gem}$ = 13.5, $J_{CH_2,2}$ = 7.4 Hz, Ar$CH_2$), 2.69 (dd, 1 H, $J_{gem}$ = 13.5, $J_{CH_2,2}$ = 6.5 Hz, Ar$CH_2$), 2.20 (m, 1 H, H5), 1.79 (m, 1 H, H5′), 1.68 (s, 3 H, Me). Minor isomer: $^1H$ NMR $\delta$ 7.33–7.17 (m, 5 H, Ar), 5.39 (m, 1 H, H5), 4.14 (m, 2 H, H6), 3.72 (dtd, 1 H, $J_{2,3}$ = 13.4, $J_{2,CH_2}$ = $J_{2,CH_2}$ = 6.6, $J_{2,3}$ = 3.4 Hz, H2),

2.96 (dd, 2 H, $J_{gem}$ = 13.5, $J_{CH_2,2}$ = 6.6 Hz, $ArCH_2$), 2.73 (dd, 2 H, $J_{gem}$ = 13.7, $J_{CH_2,2}$ = 6.5 Hz, $ArCH_2$), 1.99 (m, 1 H, H3), 1.79 (m, 1 H, H3′), 1.65 (s, 3 H, Me); IR (film) $\nu$ 2963, 2914, 2854, 1495, 1454, 1120, 1088, 751, 702 $cm^{-1}$; MS (CI, $NH_3$) $m/e$ 206 (M + $NH_4^+$), 189 (M + $H^+$). Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.10; H, 8.61.

**2i″**, an analytically pure sample could not be obtained; thus, only $^1H$ and $^{13}C$ NMR data are reported: $^1H$ NMR $\delta$ 7.30–7.19 (m, 5 H, Ar), 3.92 (dt, 1 H, $J_{3,3'}$ = $J_{3,4}$ = 8.7, $J_{3,4'}$ = 2.6 Hz, H3), 3.40 (m, 1 H, H3′), 3.05 (d, 1 H, $J_{gem}$ = 15.4 Hz, $ArCH_2$), 2.91 (d, 1 H, $J_{gem}$ = 15.4 Hz, $ArCH_2$), 1.98 (m, 2 H, H4), 1.25 (s, 3 H, Me), 1.08 (d, 1 H, $J_{6,6'}$ = 6.2 Hz, H6), 0.33 (d, 1 H, $J_{6',6}$ = 6.2 Hz, H6′); $^{13}C$ NMR $\delta$ 139.37 ($C_{ipso}$), 128.94 (2 C), 128.18 (2 C), 126.01, 70.72 (C1), 64.57 (C3), 37.12, 35.54, 25.53 (C5), 18.49, 18.40.

**Thermolysis of 1j.** **1j** (860 mg, 2.00 mmol was heated to 120 °C for 21 h in 20 mL of benzene followed by air oxidation (24 h) to give, after flash chromatography (16 × 2 cm column, hexane:$Et_2O$, 96:4), first 98 mg (0.41 mmol, 21%) of **2j** contaminated with eicosane followed by 275 mg (1.16 mmol, 58%) of an inseparable 15:41:26:18 mixture of **2j**:**2j′**(5,6-dihydro):**2j′**(2,3-dihydro):**2j″**. The products could not be purified further (radial chromatography, flash chromatography, preparative TLC, or short path distillation). $^1H$ NMR spectra of the mixture support the proposed products.

Partial $^1H$ NMR $\delta$ **2j** 4.31 (d, 1 H, $J_{3,4}$ = 2.7 Hz, H3), 3.96 (ddd, 1 H, $J_{6,6'}$ = 10.7, $J_{6,5}$ = 6.0, $J_{6,5'}$ = 3.4 Hz, H6), 3.85 (ddd, 1 H, $J_{6',6}$ = 10.6, $J_{6',5'}$ = 8.8, $J_{6',5}$ = 2.7 Hz, H6′), 0.97 (d, 3 H, $J$ = 6.9 Hz, Me); **2j′** major (assigned as 2-decyl-5,6-dihydro-4-methyl-1*H*-pyran) 5.34 (m, H3); **2j′** minor (assigned as 2-decyl-2,3-dihydro-4-methyl-6*H*-pyran) 5.39 (m, H5); **2j″** 0.10 (dd, $J$ = 6.1, 1.3 Hz).

**Thermolysis of 1k.** **1k** (388 mg, 1.00 mmol) in 20 mL of benzene was heated to 144 °C for 87 h. The solvent was removed, and the residue was flash chromatographed on a 16 × 2 cm column, eluting with hexane to give 171 mg (0.44 mmol, 44%) of starting material as an orange oil.

**2-Aza-*N*,5-dimethyl-1-phenylbicyclo[3.1.0]hexane (2l).** Thermolysis of 786 mg (2.13 mmol) of **1l** in 20 mL of benzene (140 °C, 21 h) followed by air oxidation (69 h) gave after filtration, solvent removal, and short path distillation (100 °C, 1 mmHg) 242 mg (1.29 mmol, 61%) of **2l** as a colorless oil. $^1H$ NMR $\delta$ 7.38–7.27 (m, 4 H, Ar), 7.20 (m, 1 H, Ar), 3.07 (m, 1 H, H3), 2.12 (s, 3 H, NMe), 1.96 (m, 3 H, H3′, H4), 1.16 (d, 1 H, $J_{6,6'}$ = 5.7 Hz, H6), 0.89 (s, 3 H, Me–C5), 0.58 (d, 1 H, $J_{6',6}$ = 5.7 Hz); $^{13}C$ NMR $\delta$ 139.32 ($C_{ipso}$), 129.19 (2 C), 127.83 (2 C), 126.44, 58.33 (C1), 51.43 (C3), 38.37, 33.66, 29.33 (C5), 18.83, 9.80; IR (film) $\nu$ 2926, 2859, 2835, 2778, 1602, 1446, 765, 724, 699 $cm^{-1}$; MS (CI, $NH_3$) $m/e$ 205 (M + $NH_4^+$), 188 (M + $H^+$), 187 ($M^+$). Anal. Calcd for $C_{13}H_{17}N$: C, 83.37; H, 9.15. Found: C, 83.25; H, 8.91.

***exo*-6-Ethyl-2-oxa-1-phenylbicyclo[3.2.0]heptan-7-one (3h) and *exo*-7-Ethyl-2-oxa-1-phenylbicyclo[3.1.1]heptan-6-one (4h).** In an oven-dried Fischer & Porter pressure vessel was dissolved 150 mg (0.39 mmol) of **1h** in 15 mL of $Et_2O$. The vessel was saturated with CO—3 cycles to ca. 100 psi of CO—and irradiated (450-W Hanovia lamp) for 17 h at room temperature under 90 psi of CO. The solvent was removed from the now colorless solution (some $Cr(CO)_6$(s) had precipitated out) on a rotary evaporator at water aspirator pressure. The crude semisolid was triturated with a few milliliters of hexane and the solution put on top of a 16 × 2.5 cm column and flash chromatographed by elution with hexane:$Et_2O$ (99:1) to give first 19 mg (0.09 mmol, 23%) of **4h** followed by 15 mg (0.07 mmol) of a 3:1 mixture of **3h**:**4h** both as colorless oils. The total yield of **4h** was 27% and of **3h** 14%. The second fraction was purified by a second chromatography using the same column and eluent. **3h**: $^1H$ NMR $\delta$ 7.36 (m, 5 H, Ar), 4.44 (ddd, 1 H, $J_{3,3'}$ = 9.2, $J_{3,4}$ = 8.0, $J_{3,4'}$ = 1.2 Hz, H3), 4.03 (ddd, 1 H, $J_{3',4}$ = 11.4, $J_{3',3}$ = 9.3, $J_{3',4'}$ = 5.7 Hz, H3′), 2.87 (dd, 1 H, $J_{5,4}$ = 7.5, $J_{5,6}$ = 5.5 Hz, H5), 2.75 (ddd, 1 H, $J_{6,CH'_2}$ = 8.8, $J_{6,CH_2}$ = 7.1, $J_{6,5}$ = 5.5 Hz, H6), 2.26 (m, 1 H, H4), 2.09 (dd, 1 H, $J_{4',4}$ = 12.5, $J_{4',3'}$ = 5.5 Hz, H4′), 1.79 (m, 1 H, $J$ = 7.3 Hz, $CH_2CH_3$), 1.64 (m, 1 H, $J$ = 8.8, 7.3 Hz, $CH'_2CH_3$), 1.02 (t, 3 H, $J$ = 7.4 Hz, $CH_2CH_3$); $^{13}C$ NMR $\delta$ 212.76 (CO), 136.00 ($C_{ipso}$), 128.52 (2 C), 128.34, 126.22 (2 C), 101.72 (C1), 69.89 (C3), 63.38 (C6), 44.75 (C5), 32.87 (C4), 22.58 ($CH_2$), 11.93 (Me); IR (film) $\nu$ 1776 $cm^{-1}$; MS (CI, $NH_3$) $m/e$ 234 (M + $NH_4^+$), 217 (M + $H^+$), 147($CH_3CH_2CH{=}CO$ + $H^+$). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.74; H, 7.26.

**4h**: $^1H$ NMR $\delta$ 7.49 (m, 2 H, Ar), 7.31 (m, 3 H, Ar), 4.24 (ddd, 1 H, $J_{3,3'}$ = 11.5, $J_{3,4}$ = 6.9, $J_{3,4'}$ = 2.6 Hz, H3), 4.02 (ddd, 1 H, $J_{3',3}$ = 11.4, $J_{3',4}$ = 10.0, $J_{3',4'}$ = 6.0 Hz, H3′), 3.18 (dd, 1 H, $J_{5,4'}$ = 5.2, $J_{5,4}$ = 1.8 Hz, H5), 2.65 (m, 1 H, $J_{4,4'}$ = 12.6, $J_{4,3'}$ = 9.7, $J_{4,3}$ = 6.9, $J_{4,5}$ = 2.3 Hz, H4), 2.49 (dtd, 1 H, $J_{4',4}$ = 12.6, $J_{4',5}$ = $J_{4,3'}$ = 5.6, $J_{4,3}$ = 2.6 Hz, H4′), 2.23 (dd, 1 H, $J_{7,CH_2}$ = 10.5, $J_{7,CH'_2}$ = 5.0 Hz, H7), 1.23 (m, 1 H, $CH_2CH_3$), 0.98 (m, 1 H, $CH'_2CH_3$), 0.74 (t, 3 H, $J$ = 7.3 Hz, $CH_2CH_3$); $^{13}C$ NMR $\delta$ 206.65 (CO), 134.60 ($C_{ipso}$), 128.20, 128.90 (2 C), 126.60 (2 C), 98.59 (C1), 63.19, 60.25, 47.93, 35.86, 22.24, 11.50; IR (film) $\nu$ 1778 $cm^{-1}$; MS (CI, $NH_3$) $m/e$ 234 (M + $NH_4^+$), 217 (M + $H^+$). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.55; H, 7.32.

***endo*-6-Ethyl-2-oxa-1-phenylbicyclo[3.2.0]heptan-7-one (3h′) and *endo*-6-Ethyl-2-oxa-1-phenylbicyclo[3.1.1]heptan-6-one (4h′).** Photolysis of 394 mg (1.04 mmol) of **1h′** in 20 mL of $Et_2O$ for 23 h, as described above, gave after flash chromatography (12 × 2 cm column, hexane:$Et_2O$, 9:1) 163 mg (0.76 mmol, 73%) of an inseparable mixture of **3h′** and **4h′** as a colorless oil. Spectral data are from the mixture. **3h′**: $^1H$ NMR $\delta$ 7.45–7.23 (m, 5 H, Ar), 4.32 (ddd, 1 H, $J_{3,3'}$ = 9.4, $J_{3,4}$ = 7.9, $J_{3,4'}$ = 1.5 Hz, H3), 3.78 (ddd, $J_{3'4}$ = 11.4, $J_{3',3}$ = 9.5, $J_{3',4'}$ = 6.0 Hz, H3′), 3.23 (m, 1 H, $J_{5,6}$ = 8.2 Hz, H5), 2.36 (m, 1 H), 2.11 (m, 1 H), 1.86–1.70 (m, 2 H), 1.45 (m, 1 H), 0.91 (t, 3 H, $J$ = 7.4 Hz, $CH_2CH_3$); $^{13}C$ NMR $\delta$ 214.55 (CO), 205.81 (CO), 135.36 ($C_{ipso}$), 135.08 ($C_{ipso}$), 128.55, 128.31; 128.07, 127.80, 125.88, 125.51, 102.63, 97.65, 70.02, 64.11, 58.62, 56.89, 41.80, 41.14, 26.88, 26.66, 16.45, 15.36, 12.30, 12.12; IR (film) $\nu$ 1778 $cm^{-1}$. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 78.09; H, 7.36.

**4h′**: $^1H$ NMR $\delta$ 7.45–7.23 (m, 5 H, Ar), 4.21 (dd, 1 H, $J_{3,3'}$ = 11.6, $J_{3,4}$ = 7.5 Hz, H3), 4.01 (dt, 1 H, $J_{3',3}$ = $J_{3',4}$ = 11.7, $J_{3',4'}$ = 5.7 Hz, H3′), 3.34 (t, 1 H, $J_{5,4}$ = $J_{5,7}$ = 5.7 Hz, H5), 2.62 (dt, 1 H, $J_{4,4'}$ = $J_{4,3'}$ = 12.3, $J_{4,3}$ = 7.6 Hz, H4), 2.11 (m, 1 H), 1.86–1.70 (m, 3 H), 1.03 (t, 3 H, $J$ = 7.4 Hz, $CH_2CH_3$).

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**Registry No.** **1a**, 129648-14-2; **1b**, 129620-44-6; **1c**, 129620-45-7; **1d**, 129620-46-8; **1e**, 129620-47-9; **1f**, 129620-48-0; **1g**, 129620-49-1; **1h**, 129620-50-4; **1h′**, 129705-35-7; **1i**, 127256-65-9; **1j**, 129620-51-5; **1k**, 127256-61-5; **1l**, 129620-52-6; **2a**, 127256-47-7; **2b**, 129620-27-5; **2c**, 129620-28-6; **2d**, 129620-29-7; **2e**, 95122-61-5; **2f**, 129620-30-0; **2g**, 2031-51-8; **2h**, 129620-31-1; **2h′**, 129705-33-5; **2h″**, 17851-50-2; **2i**, 129620-32-2; **2i′**, 129620-43-5; **2″**, 129620-33-3; **2j**, 129620-34-4; **2j′**, 129620-41-3; **2j″**, 129620-35-5; **2l**, 129620-36-6; **3h**, 129620-37-7; **3h′**, 129620-39-9; **4h**, 129620-38-8; **4h′**, 129705-34-6; $[(CO)_5CrC(O)C_{10}H_{21}][NMe_4]$, 129620-54-8; $(CO)_5CrC(NHCH_2CH_2C(CH_3){=}CH_2)Ph$, 129620-55-9; $[(CO)_5CrC(O)Ph][NMe_4]$, 15975-90-3; $Cr(CO)_6$, 13007-92-6; $BrNMe_4$, 64-20-0; 3-buten-1-ol, 627-27-0; 4-methyl-3-penten-1-ol, 763-89-3; 4-hexen-1-ol, 6126-50-7; *trans*-3-hexen-1-ol, 928-97-2; *cis*-3-hexen-1-ol, 928-96-1; decyllithium, 4416-59-5; 1-amino-3-methyl-3-butene, 13296-27-0; 3-methyl-3-buten-1-ol, 763-32-6.