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Photoreactions of γ,δ-Unsaturated Chromium Carbene Complexes

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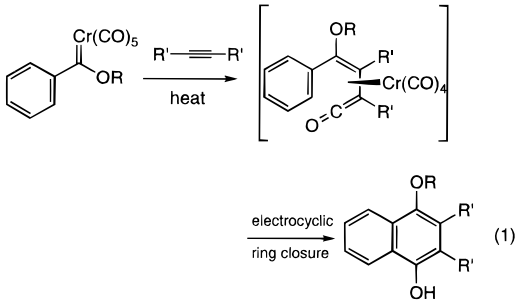
Abstract: A number of functionalized γ,δ-unsaturated chromium carbene complexes were synthesized, and their photochemistry was studied. Photolysis of carbene complexes **5** and **17** induced intramolecular [2 + 2] cycloaddition to afford cyclobutanones **6** and **18**, respectively. If the photoreactions were not run in thoroughly degassed solvents, small amounts of lactones **7** and **19** were obtained as well. Cyclobutanones **6** and **18** were stable once isolated, but underwent an acid-catalyzed Pinacol rearrangement/hydrolysis transformation in acidic solution to afford novel α-hydroxy-substituted bicyclo[3.1.0]hexanone compounds **20** and **21**. Photolysis of cyclopropyl carbene complex **28** induced a vinylcyclopropyl rearrangement involving the photogenerated ketene moiety to provide α-alkoxy cyclopentenone **29**.

Introduction

The use of chromium carbene complexes as substrates in pericyclic reactions has become accepted as an important method for the synthesis of natural products. One of the most notable developments has been the use of chromium carbene complexes in benzannulation reactions, allowing for convergent syntheses of complex aromatic systems.[1] Thermally driven benzannulation reactions based on alkyne cycloadditions to chromium carbene complexes were first reported in 1975[2] and have found many applications since then in the synthesis of *p*-alkoxyphenols and 1,4-quinones (eq 1).[3] More recently, photochemically driven benzannulation reactions of chromium carbene complexes have provided an efficient route to *o*-alkoxy- or amino-substituted phenolic products (eq 2).[4]

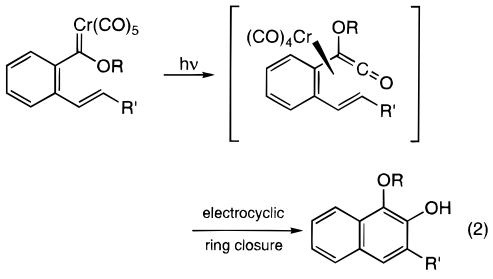
The proposed reaction mechanisms of these benzannulation reactions all involve as the key step the electrocyclic ring closure of a dienyl ketene intermediate, leading to the formation of a new aromatic ring. In contrast, pericyclic reactions of α,*β-saturated*, γ,δ-unsaturated ketenes have remained relatively unexplored.[5] As shown in eq 3, it was envisioned that such an intermediate, photochemically derived from chromium carbene

Thermal benzannulation



(1)

Photochemical benzannulation



(2)

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1996.

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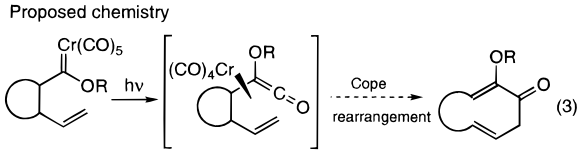
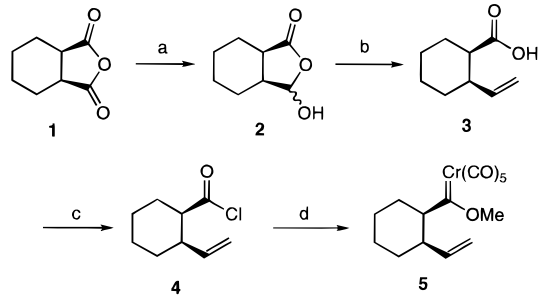
complexes, would be an amenable substrate for sigmatropic Cope rearrangement. A saturated ring system in the α,β-position would result, not in a benzannulation process, but rather in the opening of the cyclic moiety to form a larger ring system as the product. The successful realization of this process would thus provide a novel entry into a variety of medium-sized cyclic compounds.



Results and Discussion

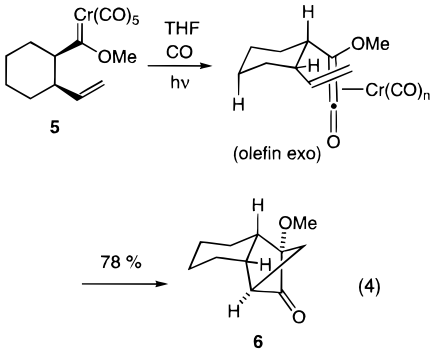
Initial experiments made use of *cis*-vinylcyclohexyl chromium carbene complex **5**, which was prepared as shown in Scheme 1. Commercially available *cis*-1,2-cyclohexanedicarboxylic

Scheme 1



Key: a) LiAlH(Ot-Bu)$_3$, 65% b) 2.2 equiv. $Ph_3P{=}CH_2$, 60% c) $(COCl)_2$, 95% d) (1) $K_2Cr(CO)_5$ (2) Me_3OBF_4, 72%.

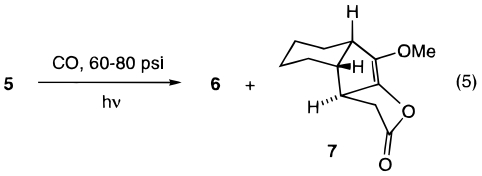
anhydride (**1**) was reduced to hydroxy lactone **2** by LiAlH(Ot-Bu)$_3$.[6] Subsequent ring opening and Wittig olefination with methylenetriphenylphosphorane afforded *cis*-carboxylic acid **3**, which underwent reaction with oxalyl chloride to cleanly provide *cis*-acid chloride **4**. Published chromium dianion chemistry[7,8] was then employed to afford the desired *cis*-carbene complex **5**. Maintenance of the *cis* disposition of the groups on the cyclohexane ring was verified by ^{1}H NMR. The signal for the methine proton α to the carbene carbon (δ 4.19) has coupling constants of 3.8, 3.8, and 10.3 Hz, consistent with one axial−axial coupling and two axial−equatorial couplings which are necessitated by the *cis* stereochemistry, assuming the large chromium moiety is in an equatorial position. Photolysis of carbene complex **5** in THF solvent under 45 psi of CO did not result in a Cope rearrangement, but rather in an intramolecular [2 + 2] cycloaddition between the ketene and olefin moieties to afford cyclobutanone **6** as a single diastereoisomer in 78% yield (eq 4). With the large metal-bound ketene group in the



equatorial position, olefin−ketene [2 + 2] cycloaddition can only occur from the energetically more favored exo rotamer of the olefin (shown) leading to **6**. The endo olefin rotamer would not be able to achieve the requisite perpendicular transition state[9] for cycloaddition and would suffer serious steric hindrance from the axial hydrogen at the 3-position. The product was identified by a characteristic cyclobutanone IR absorbance at 1787 cm^{-1}, as well as a ^{13}C NMR signal for the carbonyl carbon at δ 200. In addition, the ^{1}H NMR signals for the bridging methylene group and adjacent methine of **6** correlated well with those reported for the parent bicyclo[2.1.1]hexan-5-one.[10]

Although similar intramolecular cycloadditions with longer tethers are well-known,[11] formation of **6** was unexpected, as the use of two-atom tethers in attempted syntheses of oxabicyclohexanones has been reported to fail.[12] Furthermore, the regiochemistry of the observed cycloaddition results from bond formation between the internal olefin carbon and the central carbon of the ketene; this is the opposite of what is expected by electronic considerations.[9] This reversal of regioselectivity is most likely due to the strain inherent in a [2.2.0] bicyclohexanone *cis*-fused to a cyclohexane ring. Attempts to favor Cope rearrangement over intramolecular cycloaddition by use of Pd(II) salts or Lewis acids as catalysts[13] resulted only in reduced yields of **6** and significant carbene complex decomposition. Conversely, attempts to disfavor cycloaddition by use of electron rich aminocarbene complexes gave no reaction at all.

Although photolysis of **5** in thoroughly degassed THF, CH_2Cl_2, or benzene solvents resulted in the formation of **6** as the sole product, the use of solvents which were not degassed produced inseperable mixtures (approximately 6:1 ratio) of **6** and a new lactone **7**, with **6** always predominating (eq 5).

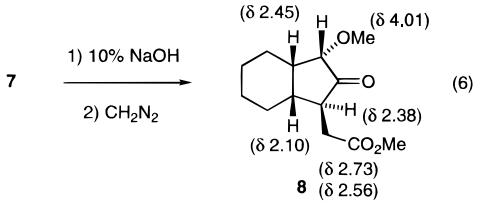


The structure of **7** was initially elusive since it is not merely a constitutional isomer of **6** but contains an additional carbon and oxygen atom, as evidenced by high-resolution exact mass spectral analysis. The ^{13}C chemical shift of δ 177 for the

(1) For reviews see: (a) Dötz, K. H. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 587. (b) Wulff, W. D. Metal Carbene Cycloadditions. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: London, 1991; Vol. 5, pp 1065−1113.
(2) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644.
(3) Dötz, K. H. *New J. Chem.* **1990**, *14*, 433. For a recent, comprehensive review see: Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, UK, 1995; Vol. 12, pp 469−547.
(4) (a) Merlic, C. A.; Xu, D. *J. Am. Chem Soc.* **1991**, *113*, 7418. (b) Merlic, C. A.; Xu, D. *J. Org. Chem.* **1993**, *58*, 538.
(5) (a) Freeman, P. K.; Kuper, D. G. *Chem. Ind.* **1965**, 424. (b) Meinwald, J.; Wahl, G. H., Jr. *Chem. Ind.* **1965**, 425.
(6) Cannone, P.; Akssira, M. *Tetrahedron* **1985**, *41*, 3695.
(7) Semmelhack, M. F.; Lee, G. R. *Organometallics* **1987**, *6*, 1839.
(8) Schwindt, M. A.; Lejon, T.; Hegedus, L. S. *Organometallics* **1990**, *9*, 2814.
(9) Valentí, E.; Pericàs, M. A.; Moyano, A. *J. Org. Chem.* **1990**, *55*, 3582.
(10) Wiberg, K. B.; Lowry, B. R.; Nist, B. J. *J. Am. Chem. Soc.* **1962**, *84*, 1594.
(11) For reviews see: (a) Snider, B. B. *Chem. Rev.* **1988**, *88*, 793. (b) Ernst, B.; DeMesmaeker, A.; Hans, G.; Veenstra, S. J. *NATO ASI Ser., Ser. C* **1989**, *273*, 207. (c) Hyatt, J. A.; Raynolds, P. W. *Org. React.* **1994**, *45*, 159.
(12) (a) Snider, B. B.; Hui, R. A. H. F. *J. Org. Chem.* **1985**, *50*, 5167. (b) Soderberg, B. C.; Hegedus, L. S.; Sierra, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 4364.
(13) Lutz, R. P. *Chem. Rev.* **1984**, *84*, 205.

carbonyl carbon, together with an IR absorbance of 1792 cm^{-1}, suggested the 5-membered lactone ring as shown; the ^{13}C spectrum also has two quaternary carbon signals at δ 137 and 125, indicative of the olefin moiety. The ^1H NMR spectrum contains signals for the methylene protons adjacent to the lactone (δ 2.64 and 2.21) which have geminal coupling constants of 17.1 and vicinal coupling constants with the adjacent methine of 11.0 and 8.4, again consistent with the rigid tricyclic ring structure of **7**. The stereochemistry of **7** follows directly from that of **6** (see Scheme 2). MM2 calculations[14] indicated that the isomer shown, with the lactone bridgehead hydrogen "down", was ≈8 kcal/mol more stable than the isomer with this hydrogen "up", and the calculated coupling constants for **7** (10.9, 7.2 Hz) more closely approximate those observed (11.0, 8.4 Hz) than do those calculated for the other isomer (12.0, 5.5 Hz).

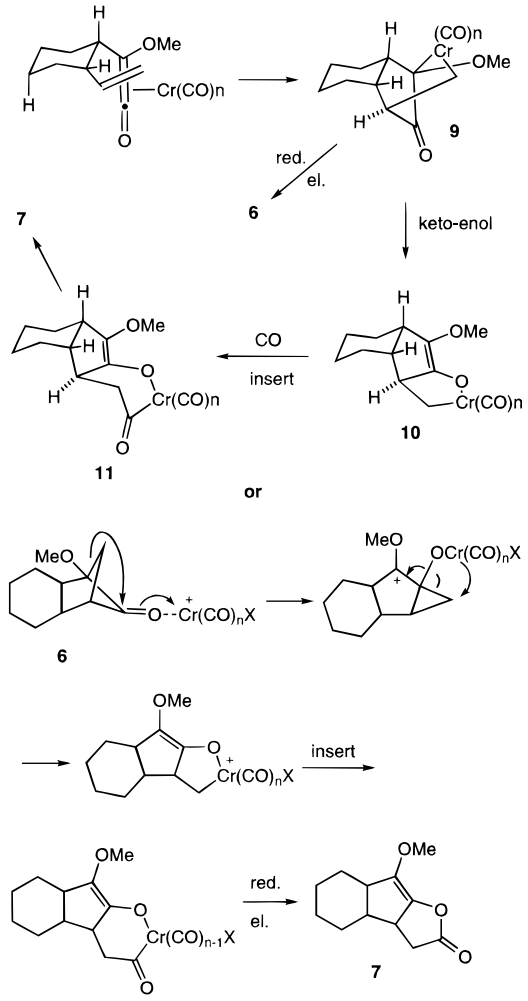
Further evidence is provided by base hydrolysis of **7**, followed by treatment with diazomethane to produce methyl ester **8** (eq 6). DQF-COSY NMR techniques established the assignments



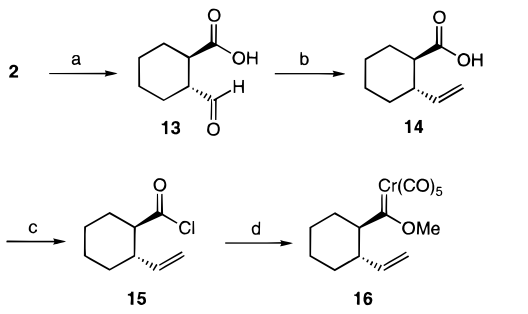
shown in eq 6, and HMBC techniques established that the ester carbonyl carbon was strongly coupled to both protons of the σ-CH_2 group (δ 2.73, 2.56) while that of the ketone coupled to the methine at δ 2.38 and much less strongly (3 bond coupling) to only the upfield proton of the σ-CH_2 group.[15] This, along with a ketone carbonyl infrared absorption at 1738 cm^{-1} (rather than 1715 cm^{-1} expected for a cyclohexanone) is more consistent with the structure shown in eq 8 than a regioisomer having a fused cyclohexanone with a β-CO_2Me group.[15] The coupling constant of 7.4 Hz between the ring-fused methine and the proton geminal to the methoxy substituent is only consistent with the methoxy group being *anti* to the bridgehead methine, since MM2[14] calculations predict a value of 7.2 Hz for this isomer and 0.8 Hz for the *syn* isomer. The relative stereochemistry of the CH_2CO_2Me group could not be unequivocally assigned. That shown is for the isomer calculated to be the more stable (≈3 kcal/mol) of the two possible isomers having the OMe group "down".

The formation of lactone **7** is mechanistically interesting and a possible pathway involving the same intermediate responsible for the production of **6** is presented in Scheme 2. Chromium-mediated ketene−olefin cycloaddition could proceed through bicyclic intermediate **9**, produced as shown in the scheme.[16] Reductive elimination would directly form the major observed product **6**. Intermediate **9** is a chromium C-enolate. Rearrangement to the O-enolate **10**, followed by insertion of CO into the chromium carbon bond,[17] would give **11**. Reductive elimination would then produce the minor product **7**. Alternatively,[15] traces of oxidized chromium residues might act as a Lewis acid, catalyzing the Pinacol rearrangement/cyclopropylcarbynyl ring opening process shown in the lower half of the scheme.

Scheme 2



Scheme 3



Key: a) 1N KOH, 99% b) 2.2 eq. $Ph_3P{=}CH_2$, 64% c) $(COCl)_2$, 94% d) (1) $K_2Cr(CO)_5$ (2) Me_3OBF_4, 58%

Further experiments made use of *trans*-carbene complex **16** which was prepared as shown in Scheme 3. The *trans* disposition of the groups on the cyclohexane ring was obtained by treatment of hydroxy lactone **2** with 1 N KOH which effected ring opening and epimerization to produce compound **13**. The

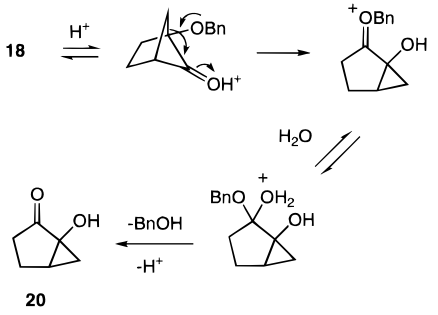
(14) Calculations were carried out on a Silicon Graphics Iris computer using Micromodel Version 4.0. Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8124. Liljefor, T.; Tai, J. C.; Li, S.; Allinger, N. L. *J. Comp. Chem.* **1987**, *8*, 1051. Sprague, J. T.; Tai, J. C.; Yuh, Y.; Allinger, N. L. *J. Comp. Chem.* **1987**, *8*, 581.

(15) NMR measurments were carried out and interpreted by Dr. Chris Rithner of this department. We thank an astute referee for suggesting structure **8** as a more reasonable structure than the 2-decalinone regioisomer originally proposed by the authors, and for suggesting an alternate mechanism for its formation.

(16) Chromium-mediated [2 + 2] cycloaddition in both ketene−olefin and ketene−imine reactions has been previously proposed to rationalize differences in stereochemistry between these reactions involving free ketenes and those involving photogenerated chromium−ketene complexes. Hegedus, L. S.; Montgomery, J.; Narukawa, Y.; Snustad, D. C. *J. Am. Chem. Soc.* **1991**, *113*, 5784.

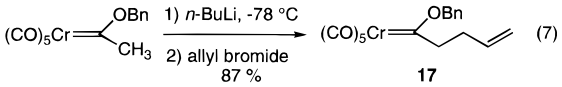
(17) Slack, D. A.; Egglestone, D. L.; Baird, M. C. *J. Organomet. Chem.* **1978**, *146*, 71.

Scheme 4



remainder of the steps were then carried out as previously described to afford **16**. The ^{1}H NMR signal for the methine proton α to the carbene carbon in **16** (δ 3.83) has coupling constants of 2.9, 11.0, and 11.0 Hz, consistent with 2 axial−axial couplings and 1 axial−equatorial coupling as expected for the *trans* diequatorial disposition of the two groups on the cyclohexane ring. Photolysis of **16** under the same conditions as used for the *cis*-carbene complex did not result in the desired Cope rearrangement, and in fact afforded a complex mixture of products, with intramolecular cycloaddition products only seen in trace amounts, and a lactone analogous to **7** not observed at all.

Photolytic reactions of the acyclic γ,δ-unsaturated chromium carbene complex **17** were also studied. To prepare **17**, the (benzyloxy)(methyl)chromium carbene complex[18] was deprotonated with *n*-BuLi at −78 °C, followed by alkylation with allyl bromide at 0 °C (eq 7).[19] The results of photolysis



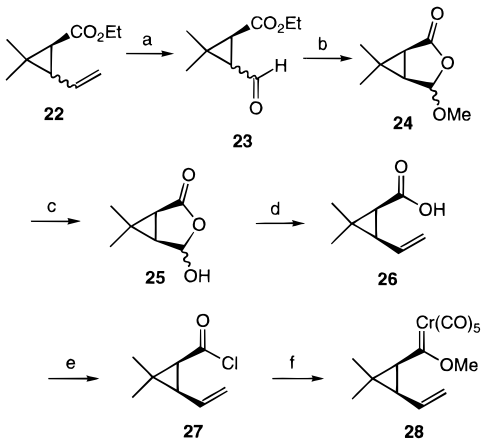
(7)

experiments with **17** mirrored those of the *cis*-carbene complex **5**. The use of carefully degassed solvents in the photolyses provided cyclobutanone **18** as the sole product, whereas photolyses using non-degassed solvents afforded inseparable mixtures of **18** as the major product and lactone **19** in minor amounts (approximately 6:1 ratio) (eq 8).

(8)

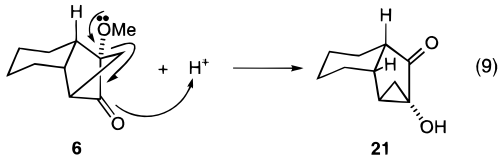
The bicyclo[2.1.1]hexanone **18**, while containing a strained ring system, is stable once isolated. However, in the presence of acidic aqueous media, **18** undergoes a facile acid-catalyzed Pinacol rearrangement and hydrolysis process to afford the α-hydroxy bicyclo[3.1.0]hexanone **20** in essentially quantitative yield (Scheme 4). This bicyclo[3.1.0]hexane system showed ^{13}C−H coupling constants characteristic for this system (t, J_{CH} = 164 Hz, cyclopropyl CH_2; d, J = 173 Hz, cyclopropyl CH; t, J = 131 Hz, cyclopentyl CH_2; t, J = 132 Hz, cyclopentyl CH_2 vs 161, 166, 130, and 130 Hz for the corresponding carbons in the parent bicyclo[3.1.0]hexane itself).[20] Similarly, the observed infrared CO stretching frequency of 1722 cm^{-1} is quite

Scheme 5



Key: a) (1) O_3, -78 °C (2) $(H_2N)_2CS$, 91% (b) NaOMe/MeOH, reflux, 40% c) H_2O/dioxane, reflux, 93% d) 2.2 eq. $Ph_3P{=}CH_2$, 80% e) $(COCl)_2$, 85% f) (1) $K_2Cr(CO)_5$ (2) Me_3OBF_4, 55%

consistent with those for related [3.1.0] systems (1710−1730 cm^{-1}),[21] compared with the normal 1750 cm^{-1} for simple cyclopentanones. A similar rearrangement took place with **6** to provide the tricyclic α-hydroxy ketone **21** (eq 9). Such contractions of four-membered rings to three-membered rings are rare, and have been of interest in the synthesis of compounds containing functionalized cyclopropyl rings.[22]



(9)

At this point, attention was turned to vinylcyclopropyl carbene complexes. It was anticipated that photogenerated vinylcyclopropyl ketene complexes would undergo more facile Cope rearrangement than would vinylcyclohexyl ketene complexes, since *cis*-1,2-divinylcyclopropanes undergo Cope rearrangements much more readily than *cis*- or *trans*-divinylcyclohexanes due to the strain present in the cyclopropyl ring.[23] Accordingly, *cis*-vinylcyclopropyl carbene complex **28** was prepared as shown in Scheme 5.

Ethyl chrysanthemate (**22**), commercially available as a mixture of *cis* and *trans* isomers, was ozonized to produce aldehyde **23**. When heated at reflux in a NaOMe/MeOH solution, **23** becomes trapped as the *cis*-methoxy lactone **24**.[24] Heating **24** at reflux in dioxane/H_2O provides hydroxy lactone **25**; ring opening and Wittig olefination with methylenetriphenylphosphorane then affords carboxylic acid **26**.[24] Transformation to acid chloride **27** with oxalyl chloride followed by chromium dianion chemistry[7,8] provides carbene complex **28**. Photolysis of **28** in CH_2Cl_2 under 60 psi of CO, however, afforded an 83% yield of α-alkoxycyclopentenone **29**, the product of a formal vinylcyclopropane rearrangement involving the ketene moiety (eq 10).

Although vinylcyclopropane rearrangements are thermally forbidden [π2s + σ2s] transformations and generally require temperatures of 200−300 °C to proceed,[25] the presence of the

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

(19) This procedure results in some dialkylation: Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1976**, *118*, 309. In our hands, typically <10% of the dialkylated product was observed, which was not problematic when carried on to subsequent steps.

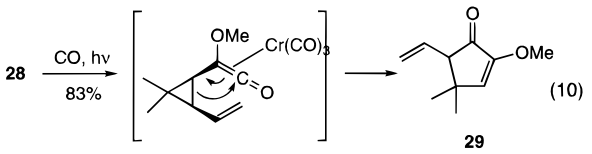
(20) Kalinowski, H.-O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; John Wiley and Sons, Ltd.: New York, 1988; p 497.

(21) See, for examples: Ziegler, F. E.; Petersen, A. K. *J. Org. Chem.* **1994**, *59*, 2707.

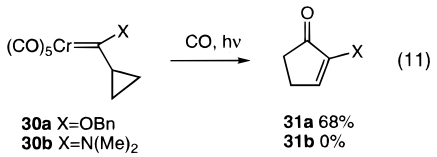
(22) See: Ihara, M.; Taniguchi, T.; Tokunaga, Y.; Fukumoto, K. *J. Org. Chem.* **1994**, *59*, 8092 and references therein.

(23) Brown, J. M.; Golding, B. T.; Stofko, J. J., Jr. *J. Chem. Soc., Chem. Commun.* **1973**, 319.

(24) Dauben, W. G.; Dinges, J.; Smith, T. C. *J. Org. Chem.* **1993**, *58* , 7635.



carbonyl π orbitals of the ketene provides a thermally allowed pericyclic [(π2s + π2s) + σ2s] reaction pathway for the cyclopropyl ketene intermediate.[26] To test the generality of this reaction, (benzyloxy)(cyclopropyl) carbene complex **30a** was photolyzed, and did in fact afford cyclopentenone **31a** as the sole product in 68% yield (eq 11). The electron rich (dimethylamino)(cyclopropyl) carbene complex **30b**[27] was likewise examined, but in this case no reaction occurred. Similar transformations of chromium carbene complexes have been explored by Herndon, in which thermally induced Cope rearrangements involving the carbene complex dπ−pπ bond are proposed as the key step in the preparation of α-alkoxy cyclopentenones.[28]



In summary, photochemically driven Cope rearrangements of chromium carbene complexes were not observed due to the presence of more favorable pericyclic reaction pathways available to the intermediate ketene species. Photolysis of acyclic and cyclohexyl γ,δ-unsaturated alkoxycarbene complexes resulted in intramolecular [2 + 2] cycloadditions to afford bicyclo[2.1.1]hexanones. Photolytic reactions performed in nondegassed solvents also afforded lactones in minor amounts as well. The bicyclohexanone compounds underwent a Pinacol rearrangement/hydrolysis transformation to afford α-hydroxy ketones. Vinylcyclopropyl carbene complexes underwent photochemically driven ketenylcyclopropyl rearrangements to produce α-alkoxy cyclopentenones.

Experimental Section

General Procedures. The 300-MHz ^{1}H NMR and 75.5 MHz ^{13}C NMR spectra were obtained on a Bruker ACE-300 spectrometer. Chemical shifts are given in ppm relative to $(CH_3)_4Si$ (0 ppm, ^{1}H) or $CDCl_3$ (77.0 ppm, ^{13}C) unless otherwise noted. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. All reactions were performed under an atmosphere of argon except as specified. Photoreactions were carried out using a 450-W 7825 medium-pressure Hg lamp immersed in a Pyrex well. The crude reaction mixtures were purified by column chromatography with silica gel (ICN Biomedicals Silitech 32−63 μm).

Materials. *cis*-Cyclohexanedicarboxylic anhydride, methyltriphenylphosphonium bromide, oxalyl chloride, ethyl chrysanthemate, and acetyl bromide were purchased from Aldrich and used as received. Trimethyloxonium tetrafluoroborate was purchased from Strem and used as received.

Hydroxy Lactone 2. This compound was prepared using a slight modification of the reported literature procedure.[6] *cis*-Cyclohexanedicarboxylic anhydride (**1**) (3.85 g, 25.0 mmol) was taken up in THF (15 mL) and cooled to −20 °C in an ethylene glycol/CO_2 bath. This was added to a −20 °C solution of $LiAlH(Ot\text{-}Bu)_3$ (7.95 g, 31.3 mmol) in THF (25 mL) via a cannula, and the resultant solution was allowed to slowly warm to room temperature with stirring over 7 h. Aqueous 10% HCl solution was then added until all solids were dissolved. The solution was extracted with CH_2Cl_2 (4 × 15 mL) and the combined organic layers were washed with brine (1 × 15 mL) and dried over $MgSO_4$. Filtration and removal of solvents under reduced pressure gave the crude product as a yellow oil. Purification via flash chromatography (SiO_2, 1/1 hexanes/EtOAc) afforded **2** (2.52 g, 65% yield) as a clear, colorless oil. The ^{1}H spectrum was consistent with that reported in the literature.[6] ^{1}H NMR δ 5.5 (br s, 1H), 4.3 (br s, 1H), 2.96 (m, 1H), 2.42−2.36 (m, 1H), 2.11−2.07 (m, 1H), 1.86−1.82 (m, 1H), 1.63−1.53 (m, 3H), 1.23−1.10 (m, 3H).

***cis*-Carboxylic Acid 3.** Methyltriphenylphosphonium bromide (3.14 g, 8.80 mmol) was taken up in THF (15 mL) under argon atmosphere and cooled to 0 °C. *n*-BuLi (5.9 mL of a 1.5 M solution in hexanes, 8.8 mmol) was added dropwise via syringe. The resultant red solution was allowed to stir at 0 °C for 30 min, and a solution of hydroxy lactone **2** (624 mg, 4.00 mmol) in THF (10 mL) was added dropwise via syringe. The solution was allowed to slowly warm to room temperature with stirring over 4 h. Aqueous 10% NaOH solution was then added until all solids had dissolved, and the solution was extracted with EtOAc (3 × 15 mL). The combined aqueous layers were treated with 3 N HCl to pH 3 and extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (1 × 10 mL) and dried over $MgSO_4$. Filtration and removal of solvents under reduced pressure gave the crude product as a yellow oil. Purification via flash chromatography (SiO_2, 4/1 hexanes/EtOAc) afforded **3** (372 mg, 60% yield) as a clear, colorless oil. ^{1}H NMR δ 11.6 (br s, 1H), 5.96 (ddd, J_1 = 7.9 Hz, J_2 = 10.4 Hz, J_3 = 17.2 Hz, 1H), 5.06 (dd, J_1 = 1.0 Hz, J_2 = 16.8 Hz, 1H), 5.02 (dd, J_1 = 1.0 Hz, J_2 = 10.3 Hz, 1H), 2.67 (m, 1H), 2.59 (ddd, J_1 = J_2 = 4.3 Hz, J_3 = 8.7 Hz, 1H), 1.82−1.67 (m, 4H), 1.59−1.52 (m, 2H), 1.43−1.32 (m, 2H); ^{13}C NMR δ 181.1, 138.2, 115.7, 45.9, 41.1, 30.1, 24.5, 24.2, 22.0; IR (neat) ν 3100−2600, 1704 cm^{-1}. Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.93; H, 8.96.

***cis*-Acid Chloride 4.** *cis*-Carboxylic acid **3** (885 mg, 5.74 mmol) was taken up in CH_2Cl_2 (10 mL), and oxalyl chloride (0.60 mL, 6.88 mmol) was added via syringe. The resultant solution was allowed to stir at room temperature for 45 min and solvents were removed under reduced pressure to give the crude product as a slightly brown oil. Purification via Kugelrohr distillation afforded **4** (897 mg, 95% yield) as a clear, colorless oil. ^{1}H NMR δ 5.91 (ddd, J_1 = 8.1 Hz, J_2 = 10.3 Hz, J_3 = 17.2 Hz, 1H), 5.15 (dd, J_1 = 1.4 Hz, J_2 = 17.2 Hz, 1H), 5.09 (dd, J_1 = 1.4 Hz, J_2 = 10.4 Hz, 1H), 3.01 (ddd, J_1 = J_2 = 4.3 Hz, J_3 = 8.9 Hz, 1H), 2.83 (m, 1H), 1.91−1.78 (m, 3H), 1.67−1.54 (m, 3H), 1.46−1.38 (m, 2H); ^{13}C NMR δ 175.1, 136.7, 116.9, 58.4, 41.5, 30.0, 25.6, 23.8, 21.9; IR (neat) ν 1795 cm^{-1}.

***cis*-Carbene Complex 5.** This carbene complex was prepared via a modification of Semmelhack and Lee's method.[7] An airless flask containing $K_2Cr(CO)_5$[8] (2.72 mmol) in THF (15 mL) was cooled to −78 °C. *cis*-Acid chloride **4** (468 mg, 2.72 mmol) in THF (5 mL) was added via syringe under argon atmosphere, and the resultant green-black mixture was stirred at −78 °C for 15 min, at 0 °C for 1.5 h, and at room temperature for 1 h. The solvents were removed under reduced pressure and the residue was taken up in chilled, degassed H_2O (20 mL). $Me_3O^+BF_4^-$ (400 mg, 2.72 mmol) was added in portions over 15 min. The solution was filtered through Celite and extracted with hexanes (5 × 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated to an orange oil. Purification via flash chromatography (SiO_2, hexanes) afforded **5** (673 mg, 72% yield) as an orange solid. ^{1}H NMR δ 5.94 (ddd, J_1 = 10.0 Hz, J_2 = 10.2 Hz, J_3 = 16.9 Hz, 1H), 4.92 (dd, J_1 = 1.8 Hz, J_2 = 10.2 Hz, 1H), 4.87 (dd, J_1 = 1.8 Hz, J_2 = 17.0 Hz, 1H), 4.70 (s, 3H), 4.19 (ddd, J_1 = J_2 = 3.8 Hz, J_3 = 10.3 Hz, 1H), 2.81 (m, 1H), 1.73−1.44+1.4−1.2 (m, 8H); ^{13}C NMR δ 366.2, 223.1, 216.5, 138.4, 114.8, 73.6, 67.2, 41.8, 32.5, 24.9, 23.6, 21.3; IR (neat) ν 2060, 1918 cm^{-1}; MS 344 (M^+).

Cyclobutanone 6. Carbene complex **5** (57 mg, 0.166 mmol) was taken up in THF (15 mL) in an airless flask equipped with a sidearm. The resultant yellow-orange solution was degassed (freeze−pump−thaw degassing using liquid N_2, 3 cycles) and transferred to an Ace

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pressure tube. The pressure tube was charged to 45 psi of CO (3 cycles) and irradiated at 25 °C for 16 h. The solvents were removed under reduced pressure, and the residue was taken up in Et_2O and decanted away from $Cr(CO)_6$. Purification of the organic layers via flash chromatography (SiO_2, 9/1 hexanes/EtOAc) afforded **6** (24 mg, 78% yield) as a clear, colorless oil. ^{1}H NMR δ 3.47 (s, 3H), 2.47 (m, 1H), 2.09 (m, 2H), 1.87 (dd, $J_1 = 3.6$ Hz, $J_2 = 6.9$ Hz, 1H), 1.62 (d, $J = 6.9$ Hz, 1H), 1.65−1.49 + 1.31−1.16 (m, 8H); ^{13}C NMR δ 199.7, 95.7, 54.6, 50.3, 35.7, 35.5, 27.9, 23.4, 20.6, 19.2, 18.8; IR (neat) ν 1787 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.46; H, 8.72.

Lactone 7. The preceding procedure was followed, except that non-degassed CH_2Cl_2 (7 mL) was used as the solvent. Irradiation for 16 h at 25 °C produced an oil which was purified by flash chromatography (SiO_2, 6/1 hexanes/EtOAc) to afford 25 mg of a 6/1 mixture of **6** and **7**. Spectral data for **7**: ^{1}H NMR δ 3.80 (s, 3H), 3.19 (m, 1H), 2.64 (dd, $J_1 = 8.4$ Hz, $J_2 = 17.1$ Hz, 1H), 2.30 (m, 1H), 2.21 (dd, $J_1 = 11.0$ Hz, $J_2 = 17.1$ Hz, 1H), the remaining cyclohexyl protons were obscured by the signals for compound **6**. ^{13}C NMR δ 177.4, 137.1, 125.1, 58.6, 44.5, 43.8, 41.1, 35.9, 29.2, 26.7, 23.5, 22.0; IR (neat) ν 1792 cm^{-1}. HRMS calcd for $C_{12}H_{16}O_3$ 208.1099, found 208.1096.

Compound 8. A mixture of **6** and **7** (90 mg) was taken up in Et_2O (10 mL), and an aqueous 10% NaOH solution (10 mL) was added. The resultant biphasic solution was allowed to stir vigorously for 2 h. The layers were separated, and the aqueous layer was acidified to pH 2 with 1 N HCl, then extracted with EtOAc (3 × 10 mL). The combined EtOAc layers were dried over $MgSO_4$, filtered, and concentrated to afford 24 mg of a slightly pink oil. This oil was taken up in freshly distilled Et_2O (15 mL), and an excess of diazomethane (>3 equiv, generated by the addition of aqueous 10% NaOH to a solution of Diazald in EtOH) was bubbled through the solution until a yellow color persisted. Argon was then bubbled through the solution for 10 min to remove excess diazomethane. The solution was concentrated to a yellowish oil and purified by flash chromatography (SiO_2, 2/1 hexane/EtOAc) to afford 9 mg of **8** as a clear, colorless oil. ^{1}H NMR δ 4.01 (d, $J = 7.2$ Hz, 1H), 3.63 (s, 3H), 3.48 (s, 3H), 2.73 (dd, $J_1 = 5.8$ Hz, $J_2 = 17.1$ Hz, 1H), 2.56 (dd, $J_1 = 3.9$ Hz, $J_2 = 17.1$ Hz, 1H), 2.50−2.35 (m, 2H), 2.15−2.05 (m, 1H), 1.76−1.52 (m, 5H), 1.34−1.11 (m, 2H), 0.97−0.79 (m, 1H); ^{13}C NMR δ 215.9, 172.1, 87.4, 58.4, 51.8, 41.6, 37.3, 33.9, 32.9, 24.9, 24.3, 21.9, 20.2; IR (neat) ν 1738; HRMS calcd for $C_{13}H_{20}O_4$ 240.1362, found 240.1362.

***trans*-Carboxylic Acid/Aldehyde 13.** Hydroxy lactone **2** (2.80 g, 17.9 mmol) was taken up in Et_2O (30 mL) and extracted with aqueous 1 N KOH solution (3 × 15 mL). The combined aqueous layers were treated with aqueous 10% HCl solution to pH 3 and extracted with CH_2Cl_2 (3 × 15 mL). These combined organic layers were washed with brine (1 × 15 mL) and dried over $MgSO_4$. Filtration and removal of solvents under reduced pressure gave the crude product as a yellowish solid. Purification via recrystallization from EtOAc afforded **13** (2.77 g, 99% yield) as a white crystalline solid, mp 217−220 °C. ^{1}H NMR δ 12.0 (br s, 1H), 9.61 (s, 1H), 2.58 (m, 2H), 2.06 (m, 2H), 1.79 (m, 2H), 1.5−1.1 (m, 4H); ^{13}C NMR δ 202.6, 181.1, 50.8, 42.4, 28.5, 25.1, 25.0, 24.8; IR (neat) ν 3400−2700, 1705. Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74. Found: C, 61.76; H, 7.76.

***trans*-Carboxylic Acid 14.** Methyltriphenylphosphonium bromide (5.69 g, 14.1 mmol) was taken up in THF (15 mL) under argon atmosphere and cooled to 0 °C. *n*-BuLi (9.4 mL of a 1.5 M solution in hexanes, 14.1 mmol) was added dropwise via syringe. The resultant red solution was allowed to stir at 0 °C for 30 min, and a solution of compound **13** (1.00 g, 6.40 mmol) in THF (10 mL) was added dropwise via syringe. The solution was allowed to slowly warm to room temperature with stirring over 6 h. Aqueous 10% NaOH solution was then added until all solids had dissolved, and the solution was extracted with EtOAc (3 × 15 mL). The combined aqueous layers were treated with 3 N HCl to pH 3 and extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (1 × 10 mL) and dried over $MgSO_4$. Filtration and removal of solvents under reduced pressure gave the crude product as a yellow oil. Purification via flash chromatography (SiO_2, 4/1 hexanes/EtOAc) afforded **14** (632 mg, 64% yield) as a clear, colorless oil. ^{1}H NMR δ 11.0 (br s, 1H), 5.68 (ddd, $J_1 = 7.4$ Hz, $J_2 = 10.3$ Hz, $J_3 = 17.4$ Hz, 1H), 5.02 dd, $J_1 = 1.7$ Hz, $J_2 = 17.3$ Hz, 1H), 4.94 (dd, $J_1 = 1.7$ Hz, $J_2 = 10.4$ Hz, 1H), 2.3−2.1 (m, 2H), 2.0−1.9 (m, 1H), 1.8−1.7 (m, 3H), 1.5−1.1 (m, 4H); ^{13}C NMR δ 181.9, 141.0, 114.5, 49.1, 43.5, 31.5, 29.3, 25.2, 25.0; IR (neat) ν 3200−2800, 1706 cm^{-1}. Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.20; H, 8.92.

***trans*-Acid Chloride 15.** *trans*-Carboxylic acid **14** (760 mg, 4.93 mmol) was taken up in CH_2Cl_2 (15 mL), and oxalyl chloride (0.54 mL, 6.16 mmol) was added via syringe. The resultant solution was allowed to stir at room temperature for 1 h and solvents were removed under reduced pressure to give the crude product as a slightly brown oil. Purification via Kugelrohr distillation afforded **15** (798 mg, 94% yield) as a clear, colorless oil. ^{1}H NMR δ 5.67 (ddd, $J_1 = 7.8$ Hz, $J_2 = 10.2$ Hz, $J_3 = 17.9$ Hz, 1H), 5.08 (dd, $J_1 = 1.1$ Hz, $J_2 = 17.2$ Hz, 1H), 5.02 (dd, $J_1 = 1.1$ Hz, $J_2 = 10.3$ Hz, 1H), 2.60 (ddd, $J_1 = 3.5$ Hz, $J_2 = J_3 = 10.8$ Hz, 1H), 2.33 (m, 1H), 2.17−2.11 (m, 1H), 1.84−1.73 (m, 3H), 1.57−1.51 (m, 2H), 1.34−1.12 (m, 3H); ^{13}C NMR δ 176.1, 139.7, 115.8, 60.4, 44.0, 31.3, 29.1, 24.9, 24.7; IR (neat) ν 1794 cm^{-1}. Anal. Calcd for $C_9H_{13}ClO$: C, 62.61; H, 7.59. Found: C, 62.42; H, 7.39.

***trans*-Carbene Complex 16.** This carbene complex was prepared via a modification of Semmelhack and Lee's method.[7] An airless flask containing $K_2Cr(CO)_5$[8] (2.06 mmol) in THF (15 mL) was cooled to −78 °C. *trans*-Acid chloride **15** (355 mg, 2.06 mmol) in THF (5 mL) was added via syringe under argon atmosphere, and the resultant green-black mixture was stirred at −78 °C for 25 min, at 0 °C for 1.5 h, and at room temperature for 1 h. The solvents were removed under reduced pressure and the residue was taken up in chilled, degassed H_2O (20 mL). $Me_3O^+BF_4^-$ (304 mg, 2.06 mmol) was added in portions over 15 min. The solution was filtered through Celite and extracted with hexanes (5 × 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated to an orange oil. Purification via flash chromatography (SiO_2, hexanes) afforded **16** (411 mg, 58% yield) as an orange oil. ^{1}H NMR δ 5.65 (ddd, $J_1 = 9.0$ Hz, $J_2 = 11.3$ Hz, $J_3 = 16.9$ Hz, 1H), 4.86 (dd, $J_1 = 1.9$ Hz, $J_2 = 11.1$ Hz, 1H), 4.84 (dd, $J_1 = 1.9$ Hz, $J_2 = 16.9$ Hz, 1H), 4.77 (s, 3H), 3.83 (ddd, $J_1 = 2.9$ Hz, $J_2 = J_3 = 11.0$ Hz, 1H), 2.25 (m, 1H), 1.92 (m, 1H), 1.81−1.63 (m, 4H), 1.28−1.22 (m, 4H), 0.98−0.83 (m, 1H); ^{13}C NMR δ 368.9, 223.3, 216.4, 141.6, 113.9, 75.6, 67.6, 46.2, 32.0, 29.5, 25.6, 25.5; IR (neat) ν 2061, 1922 cm^{-1}; MS 344 (M^+).

Carbene Complex 17. [(Benzyloxy)(methyl)carbene]pentacarbonyl chromium(0)[16] (800 mg, 2.45 mmol) was taken up in THF (20 mL) under argon and cooled to −78 °C. *n*-BuLi (1.52 mL of a 1.6 M solution in hexanes, 2.45 mmol) was added via syringe, and the resultant solution was allowed to stir at −78 °C for 30 min. Allyl bromide (0.23 mL, 2.70 mmol) was added in one portion via syringe. The solution was allowed to warm to 0 °C and stirred for 2 h. The reaction was quenched by addition of wet Et_2O (5 mL) and concentrated to an orange oil. Purification via flash chromatography (SiO_2, hexanes) afforded **17** (779mg, 87% yield) as an orange oil. ^{1}H NMR δ 7.46 (br s, 5H), 6.01 (s, 2H), 5.71 (dddd, $J_1 = J_2 = 6.5$ Hz, $J_3 = 10.2$ Hz, $J_4 = 16.8$ Hz, 1H), 4.97 (d, $J = 17.2$ Hz, 1H), 4.96 (d, $J = 10.2$ Hz, 1H), 3.46 (t, $J = 7.5$ Hz, 2H), 2.21 (q, $J = 7.3$ Hz, 2H); ^{13}C NMR δ 360.0, 223.0, 216.3, 136.2, 133.9, 129.3, 128.9, 128.5, 115.8, 83.7, 62.0, 30.4; IR (neat) ν 2061, 1951 cm^{-1}; MS 366 (M^+).

Bicyclo[2.1.1]hexanone 18. Carbene complex **17** (98 mg, 0.268 mmol) was taken up in freshly distilled THF (10 mL) in a flame-dried airless flask equipped with a sidearm. The orange solution was degassed (freeze−pump−thaw degassing using liquid N_2, 3 cycles) and transferred to a flame-dried Ace pressure tube. The pressure tube was charged to 80 psi of CO and irradiated for 21 h at 25 °C. The solution was concentrated to an oil and purified via flash chromatography (SiO_2, 3/1 hexanes/EtOAc) to afford **18** (30 mg, 57% yield) as a clear, colorless oil. ^{1}H NMR δ 7.38−7.27 (m, 5H), 4.86 (d, $J = 11.4$ Hz, 1H), 4.67 (d, $J = 11.4$ Hz, 1H), 2.56 (m, 1H), 1.92−1.84 (m, 5H), 1.80 (m, 1H), 1.58 (d, $J = 7.2$ Hz, 1H); ^{13}C NMR δ 200.1, 137.6, 128.3, 127.7, 127.5, 91.8, 69.3, 44.9, 30.1, 23.5, 21.6; IR (neat) 1791 cm^{-1}. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.43; H, 6.89.

Lactone 19. The preceding procedure was followed, except that non-degassed CH_2Cl_2 (7 mL) was used as the solvent. Irradiation for 18 h at 25 °C produced an oil which was purified via flash chromatography (SiO_2, 5/1 hexanes/EtOAc) to afford 30 mg of a 6/1 mixture of **18** and **19**. Spectral data for **19**: ^{1}H NMR δ 7.36−7.29 (m, 5H), 5.14 (d, $J = 11.7$ Hz, 1H), 5.08 (d, $J = 11.7$ Hz, 1H), 3.29

(m, 1H), 2.69 (m, 1H), 2.67 (dd, $J_1 = 8.2$ Hz, $J_2 = 16.9$ Hz, 1H), 2.34 (ddd, $J_1 = 1.7$ Hz, $J_2 = 9.2$ Hz, $J_3 = 15.0$ Hz, 1H), 2.26 (dd, $J_1 = 11.4$ Hz, $J_2 = 16.9$ Hz, 1H), 2.14 (ddd, $J_1 = J_2 = 6.2$ Hz, $J_3 = 12.4$ Hz, 1H), 1.65 (m, 1H); ^{13}C NMR δ 177.1, 136.9, 130.1, 128.0, 127.8, 127.4, 126.1, 72.6, 40.9, 37.3, 32.6, 28.5; IR (neat) ν 1792 cm^{-1}.

Bicyclic Ketone 20. Bicyclohexanone **18** (101 mg, 0.500 mmol) was taken up in wet Et_2O and added to a 10% aqueous HCl solution. The resultant biphasic solution was allowed to stir vigorously overnight. The solution was then extracted with Et_2O (3 × 10 mL) and the combined organic layers were dried over $MgSO_4$. Filtration and removal of solvents under reduced pressure gave the crude product as a clear, slightly yellow oil. Purification via flash chromatography (SiO_2, 3/1 hexanes/EtOAc) afforded **20** (54 mg, 96% yield) as a clear, colorless oil. ^{1}H NMR δ 4.24 (br s, 1H), 2.24−2.16 (m, 1H), 2.14−2.05 (m, 3H), 1.81−1.76 (m, 1H), 1.51 (dd, $J_1 = 8.4$ Hz, $J_2 = 5.4$ Hz, 1H), 1.18 (dd, $J_1 = J_2 = 5.4$ Hz, 1H); ^{13}C NMR δ 214.1, 66.8, 30.4, 28.6, 21.1, 21.0; IR (neat) ν 3399, 1722 cm^{-1}. Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.20; H, 7.00.

Tricyclic Ketone 21. Cyclobutanone **6** (26 mg, 0.144 mmol) was taken up in Et_2O (10 mL) and added to a 10% aqueous HCl solution (10 mL). The resultant biphasic solution was allowed to stir vigorously overnight. The solution was then extracted with Et_2O (3 × 10 mL), and the combined organic layers were dried over $MgSO_4$. Filtration and removal of solvents under reduced pressure gave the crude product as a clear, slightly yellow oil. Purification via flash chromatography (SiO_2, 2/1 Et_2O/hexanes) afforded **21** (23 mg, 96% yield) as a clear, colorless oil. ^{1}H NMR δ 3.59 (s, 1H), 2.30−2.26 (m, 1H), 2.18−2.07 (m, 2H), 2.01−1.92 (m, 2H), 1.56−1.47 (m, 3H), 1.45−1.41 (m, 1H), 1.34−1.23 (m, 1H), 1.08−0.97 (m, 3H); ^{13}C NMR δ 213.4, 65.8, 38.8, 35.0, 34.4, 32.1, 23.8, 22.7, 22.1, 21.4; IR (neat) ν 3383, 1717 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.17; H, 8.33.

Compound 23. This compound was prepared via a modification of the literature procedure.[24] Ethyl chrysanthemate (**22**) (2.00 g, 10.2 mmol) was taken up in freshly distilled CH_2Cl_2 (15 mL). The solution was cooled to −78 °C and ozonized oxygen was bubbled through until a blue color persisted (ca. 25 min). Argon was bubbled through until the solution became colorless (ca. 15 min). The solution was then added to a 0 °C stirring solution of thiourea[29] (388 mg, 5.10 mmol) in MeOH. After the solution was stirred for 3 h, the thiourea *S*-dioxide precipitate was filtered off and the solvents were removed under reduced pressure. The residue was taken up in Et_2O and washed with 5% aqueous $NaHCO_3$ (2 × 15 mL) and H_2O (2 × 15 mL). The organic layers were dried over $MgSO_4$, filtered, and concentrated to a yellow oil. Purification via Kugelrohr distillation afforded **23** (1.58 g, 91% yield) as a clear, colorless oil. The ^{1}H spectrum was consistent with that reported in the literature.[24] ^{1}H NMR δ *trans*: 9.53 (d, $J = 3.4$ Hz, 1H), 4.12 (m, 2H), 2.40 (m, 2H), 1.30 (s, 3H), 1.26 (s, 3H), 1.23 (t, $J = 7.2$ Hz, 3H); *cis*: 9.70 (d, $J = 6.5$ Hz, 1H), 4.12 (m, 2H), 2.08 (d, $J = 8.7$ Hz, 1H), 1.79 (dd, $J_1 = 6.5$ Hz, $J_2 = 6.6$ Hz, 1H), 1.56 (s, 3H), 1.24 (t, $J = 7.2$ Hz, 3H), 1.23 (s, 3H).

Methoxy Lactone 24. This compound was prepared via a slight modification of the literature procedure.[24] To an oven-dried 25-mL two-necked round-bottomed flask equipped with a stirbar, reflux condenser, and argon flow was added MeOH (10 mL). Sodium metal (344 mg, 14.9 mmol) was added in small portions, and the solution was heated to reflux for 30 min. A solution of **23** (1.25 g, 7.34 mmol) in MeOH (3 mL) was added via syringe, and the solution was heated to reflux for 3 h, during which time it became orange/brown in color. The solution was cooled to 0 °C and 3 N HCl was slowly added to pH 4. The solution was extracted with Et_2O (4 × 15 mL), and the combined organic layers were washed with 5% aqueous $NaHCO_3$ (3 × 15 mL) and H_2O (2 × 10 mL), and dried over $MgSO_4$. Filtration and removal of solvents under reduced pressure afforded the crude product as a yellow oil. Purification via flash chromatography (SiO_2, 4/1 hexanes/EtOAc) afforded **24** (461 mg, 40% yield) as a clear, colorless oil. The ^{1}H NMR was consistent with that reported in the literature.[24] ^{1}H NMR δ 5.01 (s, 1H), 3.46 (s, 3H), 2.01 (d, $J = 5.7$ Hz, 1H), 1.97 (d, $J = 5.8$ Hz, 1H), 1.14 (s, 3H), 1.12 (s, 3H).

Hydroxy Lactone 25. This compound was prepared according to the literature procedure.[24] Methoxy lactone **24** (621 mg, 3.98 mmol) was taken up in H_2O (5 mL) and dioxane (10 mL) and heated to reflux for 2.5 h. The solvents were removed under reduced pressure, and the residue was taken up in EtOAc and dried over $MgSO_4$. Filtration and removal of solvents under reduced pressure afforded the crude product as a yellow oil. Purification via flash chromatography (SiO_2, 2/1 hexanes/EtOAc) afforded **25** (525 mg, 93% yield) as a white crystalline solid, mp 86−89 °C (lit.[29] mp 83.5-87 °C). The ^{1}H spectrum was consistent with that reported in the literature.[24] ^{1}H NMR δ 5.43 (s, 1H), 2.05 (s, 2H), 1.13 (s, 3H), 1.12 (s, 3H).

Carboxylic Acid 26. This compound was prepared via a modification of the literature procedure.[24] Methyltriphenylphosphonium bromide (2.90 g, 8.12 mmol) was taken up in dry THF (15 mL) and cooled to 0 °C. *n*-BuLi (5.42 mL of a 1.5 M solution in hexanes, 8.12 mmol) was added via syringe, and the resultant red solution was allowed to stir 30 min at 0 °C. A solution of hydroxy lactone **25** (525 mg, 3.69 mmol) was added dropwise via syringe, and the solution was allowed to slowly warm to room temperature with stirring over 13 h. The reaction was quenched by addition of 10% aqueous NaOH until all the solids had dissolved. The solution was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with additional 10% aqueous NaOH. The combined aqueous layers were treated with 3 N HCl to pH 3 and extracted with EtOAc (3 × 15 mL). These organic layers were washed with brine (2 × 10 mL) and dried over $MgSO_4$. Filtration and removal of solvent under reduced pressure afforded the crude product as a yellow oil. Purification via flash chromatography (SiO_2, 3/1 hexanes/EtOAc) afforded **26** (413 mg, 80% yield) as a white crystalline solid, mp 49−52 °C (lit.[30] mp 47−51 °C). The ^{1}H spectrum was consistent with that reported in the literature.[23] ^{1}H NMR δ 11.9 (br s, 1H), 6.06 (ddd, $J_1 = J_2 = 10.0$ Hz, $J_3 = 17.1$ Hz, 1H), 5.19 (dd, $J_1 = 2.1$ Hz, $J_2 = 17.1$ Hz, 1H), 5.06 (dd, $J_1 = 2.1$ Hz, $J_2 = 10.4$ Hz, 1H), 1.88 (dd, $J_1 = J_2 = 9.1$ Hz, 1H), 1.68 (d, J = 8.6 Hz, 1H), 1.27 (s, 3H), 1.18 (s, 3H).

Acid Chloride 27. Carboxylic acid **26** (91 mg, 0.649 mmol) was taken up in CH_2Cl_2 (5 mL) and oxalyl chloride (85 μL, 0.973 mmol) was added via syringe. The solution was allowed to stir for 1 h, after which time the solvents were removed under reduced pressure to afford the crude product as a slightly brown oil. Purification via Kugelrohr distillation afforded **27** (88 mg, 85% yield) as a clear, colorless oil. ^{1}H NMR δ 5.86 (ddd, $J_1 = 9.5$ Hz, $J_2 = 10.3$ Hz, $J_3 = 17.0$ Hz, 1H), 5.26 (dd, $J_1 = 1.7$ Hz, $J_2 = 17.0$ Hz, 1H), 5.15 (dd, $J_1 = 1.7$ Hz, $J_2 = 10.3$ Hz, 1H), 2.30 (d, $J = 8.2$ Hz, 1H), 2.16 (dd, $J_1 = J_2 = 8.8$ Hz, 1H), 1.26 (s, 3H), 1.25 (s, 3H); ^{13}C NMR δ 169.0, 130.6, 118.6, 43.1, 42.0, 33.1, 28.1, 14.6. Anal. Calcd for $C_8H_{11}OCl$: C, 60.57; H, 6.99. Found: C, 60.80; H, 6.98.

Carbene Complex 28. This carbene complex was prepared via a modification of Semmelhack and Lee's method.[7] An airless flask containing $K_2Cr(CO)_5$[8] (1.90 mmol) in THF (15 mL) was cooled to −78 °C. Acid chloride **27** (301 mg, 1.90 mmol) in THF (3 mL) was added via syringe under argon, and the resultant green-black mixture was allowed to stir at −78 °C for 20 min. The mixture was warmed to room temperature over 2 h, and the solvents were removed under reduced pressure. The residue was taken up in chilled, degassed H_2O (20 mL), and $Me_3O^+BF_4^-$ (281 mg, 1.90 mmol) was added over 15 min. The solution was filtered through Celite and extracted with hexanes (5 × 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated to an orange oil. Purification via flash chromatography (SiO_2, hexanes) afforded **28** (346 mg, 55% yield) as an orange solid. ^{1}H NMR δ 5.95 (ddd, $J_1 = 9.5$ Hz, $J_2 = 10.2$ Hz, $J_3 = 17.0$ Hz, 1H), 5.14 (dd, $J_1 = 1.6$ Hz, $J_2 = 17.0$ Hz, 1H), 5.02 (dd, $J_1 = 1.6$ Hz, $J_2 = 10.2$ Hz, 1H), 4.71 (s, 3H), 3.59 (d, $J = 7.7$ Hz, 1H), 2.31 (dd, $J_1 = 7.8$ Hz, $J_2 = 9.3$ Hz, 1H), 1.38 (s, 3H), 1.15 (s, 3H); ^{13}C NMR δ 354.2, 223.5, 216.7, 133.0, 116.4, 66.2, 61.3, 49.2, 39.7, 29.6, 15.3; IR (neat) ν 2059, 1918 cm^{-1}; MS 330 (M^+).

Cyclopentenone 29. Chromium carbene complex **28** (60 mg, 0.182 mmol) was taken up in CH_2Cl_2 (7 mL) in an airless flask equipped with a sidearm. The resultant yellow-orange solution was degassed (freeze−pump−thaw degassing using liquid N_2, 3 cycles) and transferred to an Ace pressure tube. The pressure tube was charged to 70 psi of CO (3 cycles) and irradiated at 25 °C for 9 h. Solvents were

(29) Gupta, D.; Somar, R.; Dev, S. *Tetrahedron* **1982**, *38*, 3013.

(30) Ortiz de Montellano, P. R.; Dinzio, S. E. *J. Org. Chem.* **1978**, *43*, 4323.

removed under reduced pressure and the residue was taken up in Et_2O and decanted away from $Cr(CO)_6$. Purification of the organic layers via flash chromatography (SiO_2, 3/1 hexanes/EtOAc) afforded **29** (25 mg, 83% yield) as a clear, colorless oil. ^{1}H NMR δ 6.16 (s, 1H), 5.61 (ddd, $J_1 = 9.2$ Hz, $J_2 = 10.2$ Hz, $J_3 = 16.9$ Hz, 1H), 5.31 (dd, $J_1 = 1.1$ Hz, $J_2 = 10.3$ Hz, 1H), 5.20 (dd, $J_1 = 0.9$ Hz, $J_2 = 16.9$ Hz, 1H), 3.67 (s, 3H), 2.76 (d, $J = 8.9$ Hz, 1H), 1.21 (s, 3H), 1.03 (s, 3H); ^{13}C NMR δ 201.7, 154.5, 135.5, 131.6, 121.0, 61.8, 56.8, 39.4, 28.7, 26.6; IR (neat) ν 1721, 1626 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.06; H, 8.29.

[(Benzyloxy)(cyclopropyl)carbene]pentacarbonylchromium (0) (30a). Tetramethylammonium ate complex $[(CO)_5Cr{=}C(O)CH(CH_2)_2]^-NMe_4^+$ [31] (2.00 g, 5.97 mmol) in 30 mL of CH_2Cl_2 was treated with acetyl bromide (0.44 mL, 5.97 mmol) at −40 °C, and the resulting mixture was stirred at −30 °C for 1 h. Benzyl alcohol (0.62 mL, 5.97 mmol) was added, and the mixture was stirred at −30 °C for an additional 1 h and then warmed to 25 °C. Removal of the solvents under reduced pressure gave the crude product as a yellow oil. Purification via flash chromatography (SiO_2, hexanes) afforded **30a** (1.67 g, 80% yield) as a yellow solid. ^{1}H NMR δ 7.46−7.38 (m, 5H), 5.94 (s, 2H), 3.53 (m 1H), 1.40 (m, 2H), 1.19 (m, 2H); ^{13}C NMR δ 351.8, 223.5, 216.8, 134.2, 129.1, 128.9, 128.2, 82.3, 41.6, 18.1; IR (neat) ν 2060, 1908; MS 352 (M^+).

Cyclopentenone 31a. [(Benzyloxy)(cyclopropyl)carbene]pentacarbonylchromium(0) (**30a**) (168 mg, 0.477 mmol) was taken up in CH_2Cl_2 (7 mL) in an airless flask equipped with a sidearm. The resultant solution was degassed (freeze−pump−thaw degassing using liquid N_2, 3 cycles) and transferred to an Ace pressure tube. The pressure tube was charged to 80 psi of CO (3 cycles) and irradiated at 25 °C for 5 h. Solvents were then removed under reduced pressure and the residue was taken up in Et_2O and decanted away from $Cr(CO)_6$. Purification of the organic layers via flash chromatography (SiO_2, 3/1 hexanes/EtOAc) afforded **31a** (43 mg, 68% yield) as a white crystalline solid, mp 62−63 °C. ^{1}H NMR δ 7.35−7.29 (m, 5H), 6.37 (t, $J = 3.0$ Hz, 1H), 4.94 (s, 2H), 2.46 (m, 2H), 2.39 (m, 2H); ^{13}C NMR δ 202.4, 156.2, 135.8, 128.7, 128.5, 128.1, 127.4, 71.6, 33.0, 21.9; IR (neat) ν 1716, 1633 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.70; H, 6.56.

(31) Prepared according to literature procedure: Fischer, E. O.; Maasböl, A. *Chem. Ber*. **1967**, *100*, 2445.

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