# Formation of Cyclobutanones by the Photolytic Reaction of $(CO)_5Cr{=}C(OMe)Me$ with Electron-Rich Olefins

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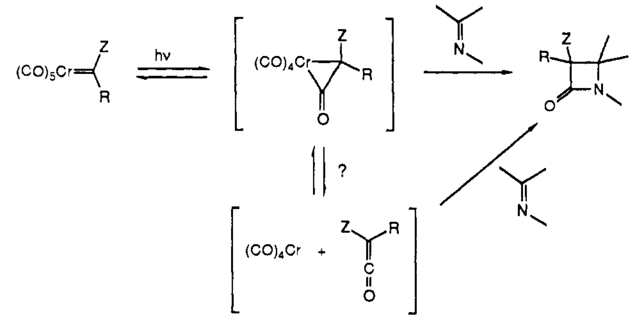
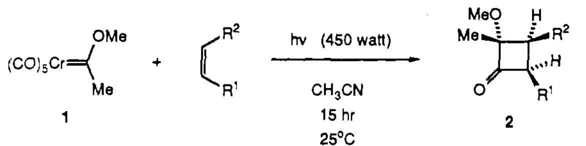
Recent research efforts in these laboratories have centered on the development of useful organic synthetic methodology based on the photolytic reactions of chromium "Fischer" carbene complexes, particularly in regards to the development of new $\beta$-lactam syntheses.[1,2] In the course of these studies it became evident that photolysis of chromium–carbene complexes resulted in the reversible production of chromium–ketene complexes, by a photochemically driven CO insertion into the chromium-carbene carbon double bond and that this unstable intermediate was responsible for $\beta$-lactam formation (eq 1).[3]



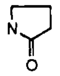
(1)

Chromium–carbene complexes such as **1** undergo thermal reactions with alkenes to produce cyclopropanes, presumably via metallacyclobutane intermediates.[4] Free ketenes react with alkenes to give cyclobutanones in a formal 2 + 2 cycloaddition process, although unactivated alkenes require forcing conditions.[5] To probe for the presence of complexed (or free) ketenes in photolytic reactions of chromium–carbene complexes, photolysis (Pyrex, 450-W Hanovia lamp) in the presence of olefins was examined, and the results are summarized in eq 2.

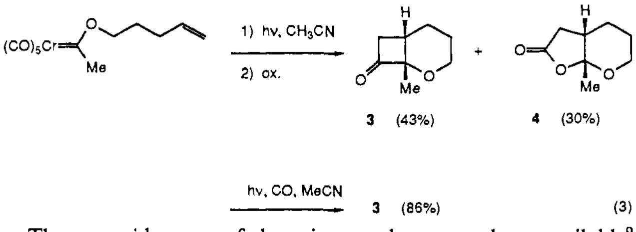
A variety of olefins were converted to cyclobutanones in good to excellent yield by this process. The crude yields, in all cases, were almost quantitative, and the crude material contained little if any byproduct. These cyclobutanones were relatively reactive and decomposed on silica gel, alumina, and flurosil, making purification by chromatography difficult. Pure material was obtained by evaporative distillation. The reaction was highly regio- and stereoselective, producing, in all cases, the single diastereoisomer shown with >95% selectivity. The regioselectivity corresponds to that resulting from attack of the more nucleophilic olefin carbon on the (electrophilic) ketene carbonyl carbon. In all cases, the methyl group of the carbene was syn to the substituent on the olefin, and the methoxy group was anti. With 1,2-disubstituted olefins (**2f**) the stereochemistry of the olefin was maintained in the cyclobutanone product. Electron poor olefins, such as methyl acrylate and acrylonitrile, did not form cyclobutanones under the same conditions.



(2)

| | | | |
|---|---|---|---|
| **2a** $R^1 = H, R^2 = OEt$ | 85% | **2d** $R^1 = H, R^2 = NHAc$ | 72% |
| **2b** $R^1, R^2 = -(CH_2)_3O-$ | 70% | **2e** $R^1 = H, R^2 = Ph$ | 30% |
| **2c** $R^1 = H, R^2 =$  | 70% | **2f** $R^1, R^2 = Me$ | 61% |

The structures and stereochemistry of **2a–f** were elucidated by spectroscopic techniques. The constitution was verified by high resolution exact mass measurements. Each compound had a strong infrared absorption at 1775–1780 cm$^{-1}$, characteristic of a four-membered carbonyl compound. High field proton and carbon NMR spectra confirmed the assigned structures as well as the absence of stereoisomers. The assigned stereochemistry for **2a–f** was confirmed by detailed NOE studies on **2b**, **2c**, and **2f**.[6] The intramolecular version of this reaction[7] was also quite efficient, producing cyclobutanone **3** in excellent yield, as a single stereoisomer (assigned cis stereochemistry by NOE measurements). Remarkably, **3** was somewhat unstable to the normal oxidative isolation procedure (see below), and up to 30% of lactone **4** was isolated when this procedure was used. Cyclobutanone **3** was the sole product when the reaction was run under carbon monoxide, and the product was purified by chromatography. The regio- and stereochemistry (syn disposition of large groups) strictly corresponds to that observed in the reaction of ethoxyketene (generated from ethoxyacetyl chloride and triethylamine) and olefins.[7,8] Thus, photolytic reactions of chromium–carbene complexes with olefins result in ketene-derived products, although the question of free versus coordinated ketene remains unresolved. The higher reactivity observed with the carbene-derived systems versus free ketenes[7] (14 h at 25 °C vs 15 h at 80–100 °C), the higher yields (60–80% vs 40–60%), the stability of the carbene complex to photolytic degradation in the absence of substrate (48 vs 15 h), and the failure to detect ketene dimers either from the reactions described above or from photodegradation in the absense of substrate, all suggest that the metal mediates these reactions in some way.



(3)

The very wide range of chromium–carbene complexes available[9] coupled with a wide variety of reactions which substituted cyclobutanones undergo[10] make the above process potentially useful

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(6) Physical data (infrared, $^1$H, $^{13}$C NMR spectra, mass spectra, exact mass measurements, and NOE and COSY data) are available as Supplementary Material.

(7) For a review of intramolecular cycloaddition reactions of ketenes with alkenes, see: Snider, B. B. *Chem. Rev.* **1988**, *88*, 793. For intramolecular alkoxyketene/alkene cycloadditions, see: Snider, B. B.; Hui, R. A. H. F. *J. Org. Chem.* **1985**, *50*, 5167. Brady, W. T.; Giang, Y. F. *J. Org. Chem.* **1985**, *50*, 5177.

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for organic synthesis. Results of similar studies with aminocarbenes promise even wider application and will be reported in due time.

A typical experimental procedure follows.

Chromium–carbene complex **1** (0.30 g, 1.20 mmol) was placed in a 30-mL Pyrex test tube which was then sealed with a rubber septum and evacuated and purged with argon (3×). *N*-Vinylacetamide (0.12 g, 1.39 mmol) in 20 mL of degassed dry acetonitrile was added by syringe, and the resulting solution was irradiated for 15 h (450-W Conrad-Hanovia 7825 medium pressure mercury lamp, Pyrex well). The solvent was then removed under vacuum, and the yellow residue was dissolved in ethyl acetate, filtered through Celite, diluted with one volume of hexane, and permitted to air oxidize overnight in a light box (6–20 W Vitalite fluorescent bulbs). Filtration of the brown suspension, solvent removal, and evaporative distillation (0.2 mm, ~120 °C) gave 0.18 g (72%) of **2d** as a colorless viscous oil.

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**Supplementary Material Available:** Full characterization and spectral data ($^1$H NMR, $^{13}$C NMR, and IR) for all new compounds (4 pages). Ordering information is given on any current masthead page.

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# Catalytic Partial Oxidation of Methane over BaPbO$_3$: Possible Involvement of Peroxide Ion

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Although numerous metal oxides catalyze the oxidative dimerization of methane to higher hydrocarbons,[1] the nature of the catalytically active sites is substantially unknown. Previous speculation that peroxide or superoxide ions are responsible for methane activation over Sm$_2$O$_3$[2] and over Na$^+$/MgO at high temperatures[3] is supported by the fact that several simple peroxides, e.g., Na$_2$O$_2$, SrO$_2$, and BaO$_2$, can stoichiometrically oxidize methane.[4] Here we show, for the first time, the existence of peroxide ions on a complex metal oxide surface that catalyzes the oxidation of methane to C$_2$ hydrocarbons. We suggest that these peroxides may exist in a novel, through-bond isomer similar electronically to ozone.[5]

**Table I.** Steady-State Methane Oxidation over BaPbO$_3$[a]

| space velocity (h$^{-1}$) | $P_{CH_4}$ (torr) | $P_{CH_4}/P_{O_2}$ | C$_2$ productivity[b] [mmol·(g cat)$^{-1}$·h$^{-1}$] | C$_2$ selectivity[c] (%) | C$_2$ yield[d] (%) |
|---|---|---|---|---|---|
| 13300 | 323 | 4.4 | 16.0 | 60.4 | 14.0 |
| 9100 | 100 | 2.4 | 6.0 | 51.8 | 18.0 |
| 10000 | 106 | 2.2 | 7.8 | 48.1 | 16.3 |
| 21100 | 100 | 2.5 | 9.4 | 68.8 | 13.7 |

[a] BaPbO$_3$ (0.35–0.55 g), 875 °C. [b] Defined as mol of CH$_4$ converted to C$_2$ products per g catalyst per h. [c] Typically, the C$_2$H$_4$/C$_2$H$_6$ ratio was 1.1. [d] The C$_3$$^+$ yield was <1%.

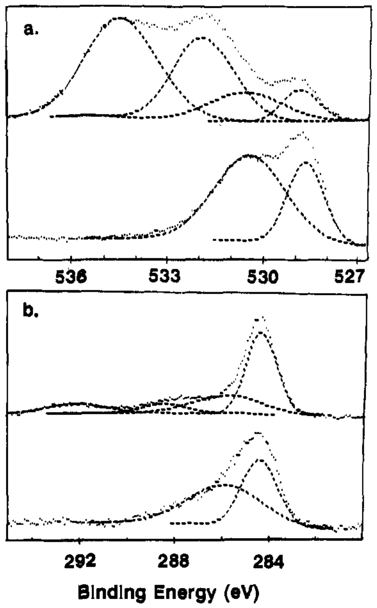

**Figure 1.** XPS spectra of unused (bottom) and used (top) BaPbO$_3$ catalysts. a. O$_{1s}$ region bottom: O$^{2-}$, 528.4 eV; O$_2$$^{2-}$, 530.1 eV; top: O$^{2-}$, 528.6 eV; O$_2$$^{2-}$, 530.3 eV; CO$_3$$^{2-}$, 531.6 eV; HCO$_3$$^-$, 534.1 eV. b. C$_{1s}$ region bottom: 284.6 eV (by definition) and 286.1, adventitious C; top: 284.6 eV (def.) and 286.1, adventitious C; CO$_3$$^{2-}$, 288.7 eV; HCO$_3$$^{2-}$, 292.3 eV.

Barium metaplumbate[6] was treated in flowing O$_2$ for several hours before beginning the oxidation reaction. As shown in Table I, moderate yields and high C$_2$ selectivities were obtained at 875 °C in a conventional 4 mm ID plug-flow reactor when the initial O$_2$ to CH$_4$ molar ratio was ~0.5. No methane oxidation was observed in similar experiments wherein quartz chips replaced the BaPbO$_3$ catalyst. These steady-state results were obtained after 2 h on stream; however, constant C$_2$ productivity was observed initially. This lack of an induction period for C$_2$ production is consistent with the hypothesis that the BaPbO$_3$ surface is responsible for the catalytic activity.

The XPS spectrum[7] of BaPbO$_3$ after annealing overnight in flowing O$_2$ at 875 °C, shown in the lowers traces of Figure 1, indicates that this material is not a typical A$^{2+}$B$^{4+}$[O$^{2-}$]$_3$ perovskite.[8] The binding energies and relative intensities (2.0:1.0)

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