Tetrahedron Letters, Vol.30, No.3, pp 295-296, 1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

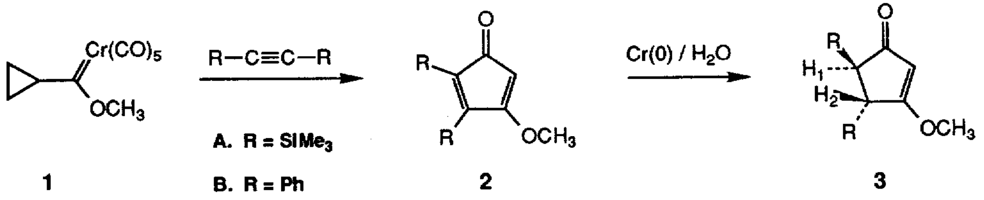
Cyclopentadienones in the Reaction of Alkynes with Cyclopropylcarbene-Chromium Complexes

James W. Herndon* and Seniz U. Turner
Department of Chemistry and Biochemistry
University of Maryland
College Park, Maryland 20742 USA

Summary: Reaction of alkynes having bulky substituents with pentacarbonyl[cyclopropyl(methoxy)methylene]chromium(0) (1) provided cyclopentadienone derivatives. Cyclopentadienones were easily hydrogenated to the corresponding cyclopentenones using chromium hexacarbonyl and water, with no problems resulting from overreduction to the cyclopentanone.

Recently, we reported that cyclopropylcarbene-chromium complexes react with alkynes to generate cyclopentenone derivatives (Scheme 1)[1]. We proposed two mechanistic schemes for the reaction, both involving reduction of cyclopentadienones as the penultimate step in the reaction. Water was required in the reaction as the source of H_1 and H_2, presumably while chromium(0) is oxidized to chromium(III). Cyclopentadienones are typically highly reactive and unstable[2], and could not be isolated from the reaction. Herein we report our attempts to isolate cyclopentadienones from the reaction, and their subsequent reduction to cyclopentenones.

Scheme 1



The reaction in Scheme 1 was typically performed in refluxing aqueous dioxane under high dilution conditions[1], however the reaction would also proceed to a lesser degree in refluxing aqueous tetrahydrofuran (THF)[1]. Given the instability of most cyclopentadienones, the milder conditions using anhydrous THF would probably be more favorable for the isolation of cyclopentadienones. A variety of stable cyclopentadienones which contain bulky substituents have been reported in the literature[2]. When carbene complex **1** was reacted with bis-trimethylsilylacetylene in refluxing THF, a compound was isolated from the reaction mixture, whose structure was assigned as 2,3-bis(trimethylsilyl)-4-methoxy-2,4-cyclopentadienone (**2A**)[3](18% yield), along with compound **3** (R=H)[4] in 6% yield. Similarly, carbene complex **1** reacted with diphenylacetylene under the same conditions to produce the cyclopentadienone **2B**[5] in 22% yield, along with cyclopentenone **3B** in 37% yield.

It was postulated earlier that chromium(0) and water is the reagent responsible for the hydrogenation reaction[1,6]. When compounds **2A** and **B** were reacted with $Cr(CO)_6$ in refluxing 1% aqueous dioxane, reduction to cyclopentenones **3** (R=H)[4] (14%) and **3B** (61%) was observed. No overreduction products were obtained from these reactions. Also, tetraphenylcyclopentadienone, a stable cyclopentadienone derivative, was readily reduced to *trans*-2,3,4,5-tetraphenyl-2-cyclopentenone (92%) under these conditions. After reduction, the reaction mixtures were intensely green, suggestive of the presence of Chromium (III) species. Neither simple enones nor 4,4-dimethyl-2,5-cyclohexadienone were reduced by this combination of reagents.

Hydrogen itself was not responsible for the hydrogenation reaction; if the reaction was performed in the presence of hydrogen gas with D_2O present, then only deuterium incorporation was observed, with minimal ^1H incorporation. Chromium hydrides, which are formed from the reaction of basic water with chromium carbonyls[6], could also be involved in the reduction reaction. Since the formation of CO_2 was minimal (0.06 eq of CO_2 / mole complex **1**), and since chromium rather than CO appears to be the reducing agent, we do not believe that metal hydrides formed from this pathway are involved in the reaction. Reduction may proceed via the intermediacy of cyclopentadienone chromium complexes[6] or may simply involve a net two-electron reduction-protonation sequence[7].

In summary we have shown that cyclopentadienones are indeed intermediates in the reaction of alkynes with cyclopropylcarbene-chromium complexes, which ultimately gives cyclopentenone derivatives. These cyclopentadienones are easily reduced to the corresponding cyclopentenones using water and $Cr(CO)_6$, with no complications from overreduction to the cyclopentanone derivatives.

Acknowledgements: We wish to thank the Petroleum Research Fund, Administered by the American Chemical Society, and the National Institutes of Health (GM-40777) for support of this research.

References:

1. Herndon, J.W.; Turner, S.U.; Schnatter, W.F.K. *J. Am. Chem. Soc.* **1988**, *110*, 3334 - 3335.

2. Ogliarusso, M.A.; Romanelli, M.G.; Becker, E.I. *Chem. Rev.* **1965**, *65*, 261 - 367.

3. Spectral data for **2A**: ^1H NMR($CDCl_3$): δ 4.68 (s, 1H); 3.79 (s, 3H); 0.25 (s, 9H); 0.23 (s, 9H). IR($CDCl_3$): 3030 (w); 2958 (s); 2940 (m); 2937 (m); 2902 (m); 1693 (s); 1604 (vs); 1291 (m); 1250 (s); 843 (s) cm^{-1}. Mass Spec (EI): 254 (M^+), 239, 182, 171, 155, 120, 105, 89, 77. Mass Spec (CI): 255 (M+1). High Res. Mass Spec: calcd. for $C_{12}H_{22}O_2Si_2$; 254.1158; found 254.1159.

4. The total reaction mixture was subjected to fluorodesilylation (KF / 5% aq. THF) prior to isolation and yield determination.

5. Spectral data for **2B**: ^1H NMR(C_6D_6): δ 7.48 - 7.53 (m, 2H); 7.21 - 7.25 (m, 2H); 6.96 - 7.06 (m, 6H); 4.57 (s, 1H); 2.96 (s, 3H). IR($CDCl_3$): δ 3059 (m); 3024 (w); 2940 (m); 1701 (vs); 1635 (m); 1586 (vs); 1345 (s); 1323 (s); 1233 (m); 972 (s) cm^{-1}. Mass Spec (EI): 262 (M); 247, 234, 221, 205, 191, 178, 130, 84.

6. Similar results have been observed earlier, but the scope and limitations of the reduction were not determined. Brown, D.A.; Hargaden, J.P.; McMullin, C.M.; Gogan, N.; Sloan, H. *J. Chem. Soc.* **1963**, 4914 - 4918. Also, these results suggest that chromium complexes preferentially to the arene rings of tetraphenylcyclopentadienone.

7. a. Cyclopentadienones are easily reduced by electron donors. Oestrich, S.; Broser, W.; Kurreck, H. *Z. Naturforsch., B.***1977**, *32B*, 686 - 692. b. For an example of rapid reduction in another cyclopentadienone-forming reaction, see Doyama, K.; Fujiwara, K.; Joh, T.; Maeshima, K.S. *Chem. Lett.* **1988**, 901 - 904.

(Received in USA 27 October 1988)