

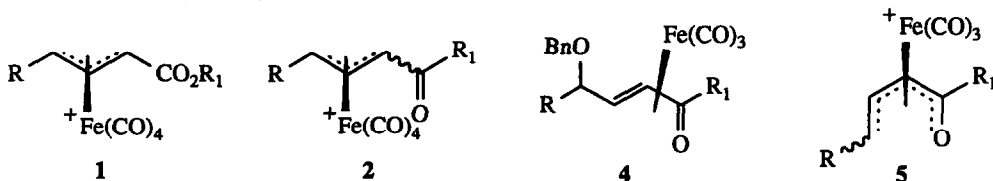
IRON CARBONYL-MEDIATED HOMOLOGOUS MICHAEL REACTIONS OF γ -ALKOXY ALKENONES

Tianhao Zhou and James R. Green*

Department of Chemistry and Biochemistry
University of Windsor, Windsor, Ontario, N9B 3P4, CANADA

Abstract: Iron tetracarbonyl complexes of γ -benzyloxy- α,β -unsaturated ketones react with several nucleophiles in the presence of Lewis acids to give γ -substitution products. The allyltetracarbonyliron cation intermediates generated allow retention of configuration of the double bond.

We have been interested in the novel synthetic applications of cationic tetracarbonyliron allyl complexes.¹ We recently reported the reactions of ester substituted members of this family (1) with masked enolates as routes to 1,6-dicarbonyl compounds.^{1a} Application of these homologous Michael reactions to ketone-substituted tetracarbonyliron allyl cations (2) is much more problematic. Foremost among these problems is the fact that ketone carbonyl attack is the dominant mode of reaction for the precursor η^2 -enone-Fe(CO)₄ complexes (i.e., 3) with Lewis acid-nucleophile combinations.² Furthermore, the facile conversion of these η^2 -tetracarbonylalkene complexes to η^4 -heterodiene complexes (i.e., 4)³ renders as a distinct possibility the formation of η^5 -oxapentadienyl complexes (5). η^5 -Oxapentadienyl complexes are unknown in iron chemistry and have a limited precedent in general,^{4,5} and present at least two different rearrangement problems.⁶



We chose γ -benzyloxy, α,β -unsaturated ketones (6) as a starting point for the investigation of these questions,⁷ the benzyloxy function being chosen in part on the basis of its expected reluctance to undergo oxidative addition to Fe(0). Subjecting an ethereal solution of 6 to Fe₂(CO)₉ under CO atmosphere led to prompt complex formation. The ¹³C NMR spectra (CDCl₃) of these complexes showed ketone carbonyls (3f, 195.8 and 195.5 ppm; 3b, 206.1 ppm), indicative of η^2 -iron tetracarbonyl complexes (3), and displayed no evidence of η^4 -heterodiene complexes (4).⁸

Complexes 3 reacted rapidly with silyl enol ethers, silyl ketene acetals, allyltributyltin, and electron rich arenes in the presence of Lewis acids, through the intermediacy of allyltetracarbonyliron cation 2, to give 7, following trimethylamine N-oxide induced decomplexation. Performing this sequence without isolation of any of the intermediates, except for removal of insoluble iron residue from 3 by filtration (and replacement of CH₂Cl₂ for Et₂O as solvent), led good yields of 7 (see Scheme 1 and Table 1).⁹

The reactions feature exclusive attack at the γ -carbon of the alkenone (C-3 of the iron allyl) for all

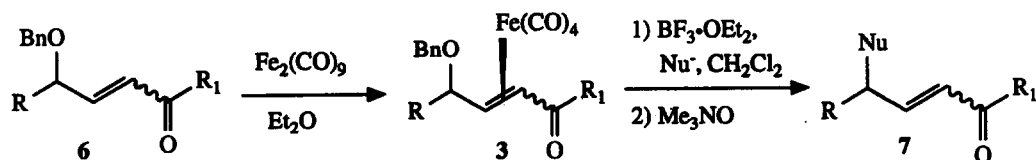
Table 1. Trapping of Ketone-Substituted Iron Allyl Cations

Substrate	Nucleophile	Product (% Yield) ^a
		(81)
		(70) ^b
		(81)
		(78)
		(62) ^c
		(82) ^c
		(52)
		(68) ^c
		(58)
		(75)
		(81)

a) Yields based on starting ketones (**6**)

b) Lewis acid = $ZrCl_4$ (-30 °C, 1h). Z/E = 97/3, based on integration of 1H NMR resonances of crude product

c) Isolated as a mixture of diastereomers



Scheme 1

nucleophiles studied, including allyltributyltin, which has been reported to give C-1 attack in a related case.¹⁰ Furthermore, essentially total retention of double bond configuration is realized with the proper choice of Lewis acid. Boron trifluoride, which was successful for the *E* disubstituted cases, caused significant amounts of isomerization for the *Z* isomers (*Z/E*=72/28). This problem was rectified by switching to ZrCl_4 , which effected the transformation with negligible isomerization (*Z/E*=97/3). The retention of double bond configuration is consistent with the known geometric stability of η^3 -allyltetracarbonyliron cations.¹¹ In none of the cases did we observe the products from competitive attack at the ketone carbonyl, from nucleophile induced deprotonation of the allyl cation,¹⁰ or from CO insertion with the nucleophile.¹² In low temperature NMR studies of a mixture of 3b (the η^2 - $\text{Fe}(\text{CO})_4$ complex of 6b) and ZrCl_4 , we did not detect any evidence a complex of either the ether or ketone oxygen to Zr, but rather a spectrum consistent with the allyl cation (*anti*-2, R=H, $\text{R}_1=\text{CH}_3$).¹³

Comparison of the reactivity of 2 with analogous ketone substituted allylpalladium complexes reveals some noteworthy distinctions.¹⁴ Although the regiochemistry of nucleophilic attack is identical in both cases, the allyliron complexes are more electrophilic species, as the nucleophiles employed here do not generally couple with allylpalladiums. Moreover, palladium allyls are not geometrically stable, which precludes their use in the preparation of (*Z*)-7.

The 1,6-dioxygenated functions generated by these transformations are of increasing synthetic importance.¹⁵ Further work on the applications of this chemistry are in progress and will be reported in due course.¹⁶

References and Notes

- (a) Green, J. R.; Carroll, M. K. *Tetrahedron Lett.* **1991**, 32, 1141. (b) Gajda, C.; Green, J. R. *Synlett* **1992**, 973.
- (a) Rybinskaya, M. I. *Pure Appl. Chem.* **1982**, 54, 145, and references therein. (b) For reactions characteristics of allylsilanes and allyltins, see Fleming, I. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 2.2. (c) For reactions characteristic of silyl enol ethers, see Chan, T.-H. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 2.3. (d) Thomas, S. E.; Danks, T. N.; Rakshit, D. *Phil. Trans. R. Soc. Lond. A* **1988**, 326, 501.
- (a) Alcock, N. W.; Danks, T. N.; Richards, C. J.; Thomas, S. *J. Chem. Soc., Chem. Commun.* **1989**, 21. (b) Cardaci, G. *J. Am. Chem. Soc.* **1975**, 97, 1412. (c) Koerner von Gustorf, E.; Grevels, F.-W.; Krüger, C.; Olbrich, G.; Mark, F.; Schulz, D.; Wagner, R. *Z. Naturforsch. B* **1972**, 27, 392. (d) Brodie, A. M.; Johnson, B. F. G.; Josty, P. L.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1972**, 2031.
- (a) Trakarnfruk, W.; Arif, A. M.; Ernst, R. D. *Organometallics* **1992**, 11, 1686. (b) Schmidt, T.;

- Goddard, R. *J. Chem. Soc., Chem. Commun.* **1991**, 1427. (c) Masters, A. P.; Richardson, J. F.; Sorensen, T. S. *Can. J. Chem.* **1990**, *68*, 2221. (d) Cheng, M.-H.; Cheng, C.-Y.; Wang, S.-L.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1990**, *9*, 1853. (e) Powell, P. *Adv. Organomet. Chem.* **1986**, *26*, 125, and references therein.
5. For unsuccessful attempts to prepare iron η^5 -oxapentadienyl complexes from their η^3 -carboxyallyliron analogues, see: Cheng, M.-H.; Wu, Y.-J.; Wang, S.-L.; Liu, R.-s. *J. Organomet. Chem.* **1989**, *373*, 119.
 6. Iron pentadienyl cations are known to undergo low temperature isomerization from S to U shaped complexes, which would result in formation of Z-7 from E-6 if applicable to these complexes. Iridium oxapentadienyl cations isomerize to hydroxypentadienyl complexes; see reference 4e.
 7. Prepared by reaction of propargyl benzyloxy acetylides with aldehydes, Red-Al[®] reduction of the alkyne (dicyclohexylborane for Z isomers) to the E alkenes, and MnO₂ or Swern oxidation to 6.
 8. The carbonyl carbon of η^4 -oxadiene complexes is normally shifted ~50 ppm upfield in the ¹³C NMR, relative to the free alkenone; (a) Brookhart, M. S.; Koszalka, G. W.; Nelson, G. O.; Scholes, G.; Watson, R. A. *J. Am. Chem. Soc.* **1976**, *98*, 8155. (b) Danks, T. N.; Rakshit, D.; Thomas, S. E. *J. Chem. Soc., Perkin Trans. I* **1988**, 2091.
 9. Typical experimental procedure: A mixture of 6a (0.1342 g, 0.706 mmol) and Fe₂(CO)₉ (0.360 g, 0.988 mmol) in Et₂O (15 mL) was stirred under CO for 2 h. After filtration through Celite[®] and concentration of the filtrate in vacuo, CH₂Cl₂ (20 mL) and cyclohexanone trimethylsilyl enol ether (0.15 mL, 0.77 mmol) were added, and the solution cooled to -30 °C under N₂. BF₃-Etherate (96 μ L, 1.1 equiv) was added, and the reaction was stirred at -30 °C for 1h, and warmed to room temperature. Aqueous Na₂CO₃ was added, followed by Me₃NO (0.3 g), and the reaction was stirred for 2 h. Following the addition of 3M HCl, a conventional workup followed by silica gel chromatographic purification (5:1 petroleum ether:Et₂O) afforded 7a (0.1030 g, 81% yield).
 10. Li, Z.; Nicholas, K. M. *J. Organomet. Chem.* **1991**, *402*, 105.
 11. (a) Gibson, D. H.; Erwin, D. K.; *J. Organomet. Chem.* **1975**, *86*, C31. (b) Dieter, J.; Nicholas, K. M. *J. Organomet. Chem.* **1981**, *212*, 107. (c) Salzer, A.; Hafner, A.; *Helv. Chem. Acta* **1983**, *66*, 1774. (d) Krivykh, V. V.; Gusev, O. V.; Petrovskii, P. V.; Rybinskaya, M. I. *J. Organomet. Chem.* **1989**, *366*, 129.
 12. See reference 2d and Yeh, M.-C. P.; Tau, S.-I. *J. Chem. Soc., Chem. Commun.* **1992**, 13.
 13. *anti*-2 (R=H, R₁=CH₃) (CD₃CN, -40 °C) δ 5.78 (m, 1H), 4.97 (d, 1H, J=7.2), 4.59 (d, 1H, J=8.1), 4.21 (d, 1H, J=13.4), 2.32 (s, 3H).
 14. (a) Collins, D. J.; Jackson, W. R.; Timms, R. N. *Aust. J. Chem.* **1977**, *30*, 2167. (b) Jackson, W. R.; Strauss, J. U. *Aust. J. Chem.* **1977**, *30*, 553. (c) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089.
 15. (a) Snider, B. B.; Shi, Z. *J. Am. Chem. Soc.* **1992**, *114*, 1790. (b) Wasserman, H. H.; Prowse, K. S. *Tetrahedron Lett.* **1992**, *33*, 5423. (c) Shimizu, I.; Nakagawa, H. *Tetrahedron Lett.* **1992**, *33*, 4957.
 16. We are grateful to NSERC Canada and the University of Windsor for financial support.

(Received in USA 23 November 1992; accepted 24 May 1993)