Lewis Acid-Promoted Addition of Allyl(cyclopentadienyl)iron(II) Dicarbonyl To Unactivated Ketones

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Abstract: The Lewis acid-promoted addition of allyl(cyclopentadienyl)iron(II) dicarbonyl (1) to unactivated ketones provides zwitterionic iron-olefin complexes 5 as isolable salts. Treatment of these complexes with NaI in wet acetone affords homoallylic alcohols in good to excellent overall yields.

Recently we introduced¹ a new aldehyde allylation strategy² utilizing allyl(cyclopentadienyl)iron(II) dicarbonyl³ (1) in which the metal moiety is retained in a potentially useful form^{4,5} within the adduct 2 (Scheme 1). Previous to this work, simple carbonyl compounds had remained notably absent from the list of carbon- and heteroelectrophiles known to react with allyliron reagent 1.⁶ We therefore questioned whether *ketones* would also



Scheme 1

participate in these Lewis acid-promoted allylation reactions.⁷ Perfluoroacetone is the only ketone reported in the literature which reacts with reagent 1, giving tetrahydrofuran 4 as a result of spontaneous ring closure of ironolefin complex 3 (top, Scheme 2).⁸ In this communication we report that, with the assistance of BF₃-etherate⁹, allyliron reagent 1 adds to <u>unactivated</u> ketones to afford <u>acyclic</u> iron-olefin complexes 5 (bottom, Scheme 2).





We have examined a number of alkyl and aromatic ketones in our studies, the results of which are summarized in the **Table**. For the purpose of evaluating the efficiency of the addition process, iron-olefin complexes **5** were converted to homoallylic tertiary alcohols **6** by treatment with NaI in acetone. In general, the allylation reactions proceed more sluggishly than those previously described¹ involving aldehydes, reaching completion after several hours in diethyl ether at room temperature using a three-to-four fold molar excess of both the allyliron reagent and Lewis acid. In most cases, the yield of alcohols **6** is good to excellent. However, the following ketones were found to be completely unreactive under these conditions and were recovered quantitatively after NaI workup: benzophenone, 4-hydroxybenzophenone, 4-hydroxyacetophenone, and 4,4'-dimethoxybenzophenone. Thus, in line with our previous observations with aldehydes, strongly electron-rich carbonyl centers fail to react with this mildly nucleophilic allyliron reagent.⁶

The following experimental procedure is representative: To a solution of the ketone (1 mmol) and BF3etherate (4 mmol) in Et₂O (10 mL) is added a solution of freshly-prepared allyliron reagent 1^3 (4 mmol) in Et₂O (5 mL). The mixture is stirred at room temperature for 12 hours. Filtration of the suspension under argon provides iron-olefin complexes 5 as crude yellow salts. Dissolution of the salts in moist acetone (20 mL) and addition of NaI (6 mmol) produces an immediate formation of FpI as evidenced by the black coloration. Evaporation and flash chromatography¹⁰ of the reaction mixture affords homoallylic alcohol 6 as a colorless-to-pale yellow oil.¹¹

The isolated iron-olefin complexes 5 appear to be relatively air-stable yellow salts which gradually darken in appearance, eventually becoming brown oils upon prolonged exposure to the atmosphere.¹² Thusfar, we have not been able to obtain complexes 5 in analytically-pure form due to the presence of an allyliron-BF₃ co-precipitate.¹³ We note that none of the [3+2]-cycloadducts 7 which might be expected to arise from complexes 5 have been detected in any of the crude reaction mixtures (Scheme 3).



Efforts are underway in our laboratory to extend this methodology to other carbon electrophiles. The diastereofacial selectivity of the allylation reaction and synthetic utility of the iron-olefin complexes are issues which we are addressing at this time. The results of these investigations will be presented in due course.

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^a Fp⁺=(cyclopentadienyl)iron(II) dicarbonyl cation

^b Isolated yields after successive flash chromatography columns, first with CH₂Cl₂ then with EtOAc:hexane.

^c Isolated yield after successive flash chromatography columns, first with CH₂Cl₂ then with acetone:CH₂Cl₂.

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- 10. It is generally necessary to carry out two successive flash columns (eluting the first column with CH₂Cl₂ and the second column with EtOAc:hexane) to remove all impurities and discoloration.
- 11. Alcohols 6 have been characterized on the basis of IR and proton NMR (300 MHz) analysis.
- 12. We attribute the formation of the oil to facile hydrolysis of the O-BF₃ bond.
- 13. This allyliron:Lewis acid adduct has been purified and characterized by IR and proton NMR spectroscopy. We intend to report on the structural and chemical properties of this compound at a later time.

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