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[3 + 2]-Cycloaddition Reactions of Allyl(cyclopentadienyl)iron(II) Dicarbonyl with Unactivated Carbonyl Compounds

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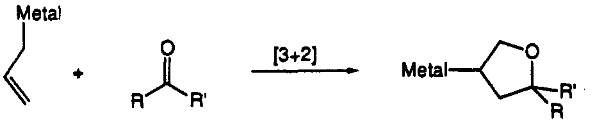
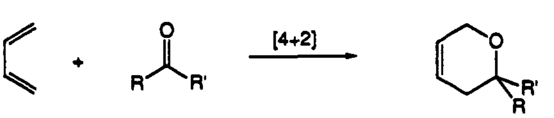
Summary: A procedure is reported for the synthesis of tetrahydrofuran esters based on a formal [3 + 2]-cycloaddition reaction of allyl(cyclopentadienyl)iron(II) dicarbonyl with carbonyl compounds.

The [3 + 2]-cycloaddition reaction of allylmetal complexes with activated double bond compounds has proven to be an attractive method for forming carbocyclic and heterocyclic rings.[1,2] However, this methodology has seldom been applied to the synthesis of five-membered oxygen rings[3] (eq 1), in contrast to the analogous [4 + 2]-cycloaddition (hetero Diels–Alder) reaction of 1,3-dienes with carbonyl compounds which has received considerable attention for the synthesis of *pyrans* (eq 2).[4] Tetrahydrofurans constitute an important class of heterocyclic compounds because of their widespread occurrence within the structures of many natural products and pharmaceutical agents as well as for their utility as building blocks for synthesis.[5-7] In this paper, we describe a procedure for the synthesis of tetrahydrofurans based on a formal [3 + 2]-cyclization reaction between allyl(cyclopentadienyl)iron(II) dicarbonyl (1)[8] and carbonyl compounds.



(1)



(2)

Over the past 30 years, σ-complex 1 and its derivatives have been studied extensively in reactions with a wide variety of organic and inorganic electrophiles.[9] Additions of 1 to multiple bond compounds X=Y result in the formation of a zwitterionic π-complex 2, which spontaneously cyclizes to a cycloadduct 3 (Scheme I). Numerous types of activated double bonds have been shown to participate in these allyliron [3 + 2] cycloadditions, including those where X=Y is C=C, C=N, C=S, S=O, and S=N. However, the carbonyl group has remained conspicuously absent from this list, with perfluoroacetone being the only carbonyl compound known to react with reagent 1 to give a tetrahydrofuran adduct.[10] In order to direct this cycloaddition chemistry toward the synthesis of furans (and related heterocycles), we set out to develop a general procedure which would enable unactivated carbonyl compounds to react efficiently with allyl(cyclopentadienyl)iron dicarbonyl complexes. Earlier we reported that stoichiometric amounts of BF_3–etherate can be used to promote the addition of σ-complex 1 to aldehydes[11] and ketones,[12] giving iron–olefin π-complexes 4 as isolable yellow precipitates. However, all attempts to convert these acyclic adducts of furans 5 proved unsuccessful, and led instead to extensive demetalation of the π-complex.

Upon further investigation, we have found that π-adducts 4 can be converted in good overall yield to furan esters 6 using a stepwise cyclization–CO insertion procedure (Scheme II). To demonstrate this methodology, we examined a number of iron–olefin complexes 4 which were prepared from aldehydes or ketones using our previously described BF_3-promoted allylation procedure.[13] The cyclization reactions are readily effected by adding 1 equiv of $K^{+-}O^tBu$[14] to the π-complex in CH_2Cl_2 at −20 °C. The progress of the reaction can be monitored spectroscopically by observing the disappearance of the

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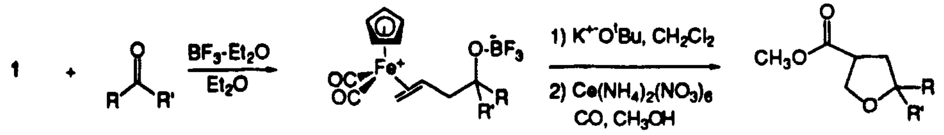
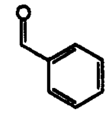
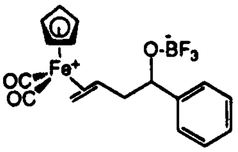
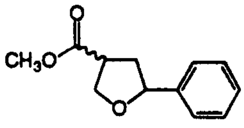
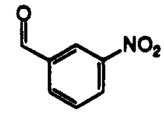
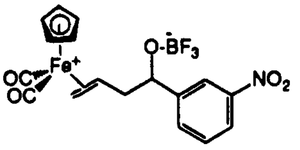
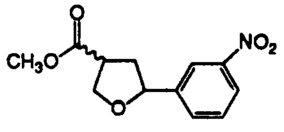
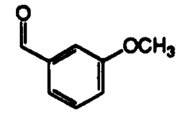
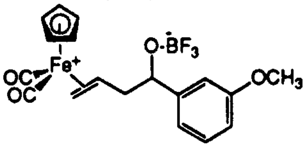
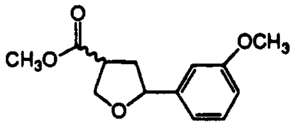
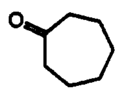
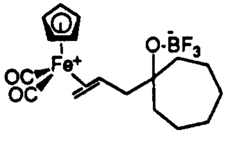
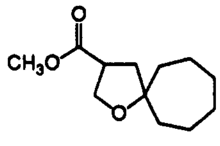
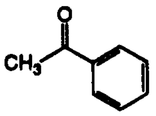
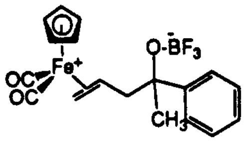
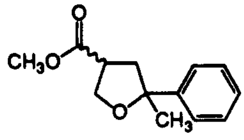
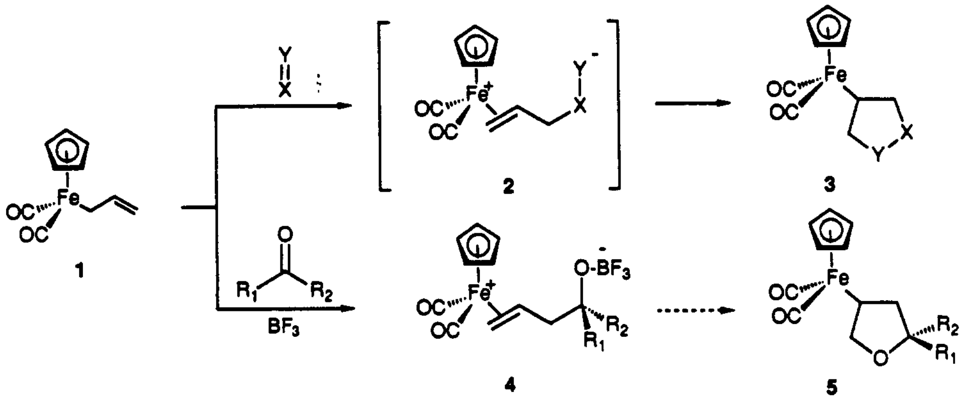
Table I. [3 + 2] Cycloadditions of Allyl(cyclopentadienyl)iron Dicarbonyl with Carbonyl Compounds



carbonyl compd	iron–olefin π-complex	cycloadduct (yield, ratio)
	 (80%)	 (45%, 1.5:1)
	 (80%)	 (43%, 1.2:1)
	 (75%)	 (45%, 1.2:1)
	 (45%)	 (19%)
	 (50%)	 (20%, 1.1:1)

Scheme I



twin CO infrared stretching bands at 2070 and 2030 cm^{-1} for π-complex 4 and the appearance of new signals at 2000 and 1945 cm^{-1} corresponding to iron σ-complex 5. Because of the difficulty in handling the somewhat sensitive cycloadducts, the crude reaction mixture is treated with a methanolic solution of ceric ammonium nitrate under an atmosphere of CO to transform iron furan 5 to furan ester 6. The combined yields for this cyclization–CO insertion procedure are 40–45% for iron–olefin complexes derived from aldehydes, while the yields are around 20% for the complexes prepared from ketones (Table I).

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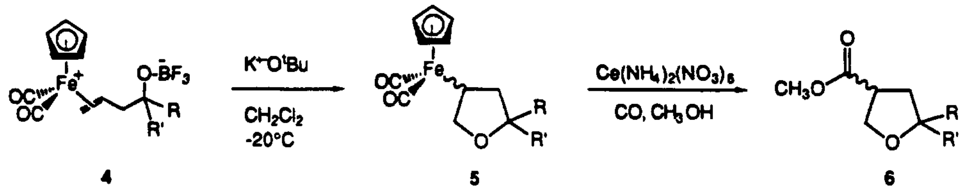
[13] The allylation procedures[11,12] we reported earlier for the preparation of homoallylic alcohols utilized an excess of the *allyliron reagent* and *Lewis acid*. Thus, the yields of homoallylic alcohols obtained from these additions were based on the amount of the starting carbonyl compound. In the present procedure, an excess of the *carbonyl compound* is used in order to obtain π-adducts 4 which are not contaminated with large amounts of an allyliron–Lewis acid coprecipitate. Consequently, the yields for the π-adducts shown in the table are based on the amount of allyliron complex 1.

[14] Tetrabutylammonium fluoride, (dimethylamino)pyridine, and sodium methoxide were also effective at promoting the cyclization.

Scheme II



In summary, a new [3 + 2]-cycloaddition route to furans has been described which is based on the BF_3-promoted reaction of allyl(cyclopentadienyl)iron(II) dicarbonyl with aldehydes and ketones. Further work is currently in progress to improve the efficiency and stereoselectivity of the cycloaddition process, and to apply this methodology to the synthesis of other heterocyclic ring systems.

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Supplementary Material Available: Textural presentation of experimental data and figures of ^1H NMR spectra for cycloadduct 6 (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the Journal, and can be ordered from the ACS. See any current masthead page for ordering information.

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(15) The following experimental procedure is representative. *Preparation of iron–olefin π-complex*: A freshly-prepared[8] solution of 1 (14 mmol) in 50 mL of Et_2O is added to a stirred mixture of benzaldehyde (3.78 g, 42 mmol) and BF_3–Et_2O (1.72 mL, 14 mmol) in 100 mL of Et_2O at 0 °C. The mixture is stirred at 0 °C for 3 h, and the yellow precipitate is collected by filtration under an Ar atmosphere, washed with anhydrous Et_2O (150 mL), and dried *in vacuo* to afford 4.21 g (80%) of the iron–olefin π-complex. *Cyclization–CO insertion reactions of π-complexes*: A mixture of the π-complex (188 mg, 0.50 mmol) and KO^tBu (62 mg, 0.55 mmol) in 10 mL of CH_2Cl_2 is cooled to -20 °C, and acetone (1 mL) is added with stirring. The mixture is allowed to stir at -20 °C for 12 h and is then added dropwise to a solution of ceric ammonium nitrate (1.37 g, 2.5 mmol) in 10 mL of anhydrous CH_3OH at -78 °C over a 0.5-h period. Stirring is continued for 30 min, and the solution is warmed to room temperature and then evaporated *in vacuo*. The crude product mixture is purified by silica gel flash chromatography, eluting first with CH_2Cl_2 and then with 2% acetone/CH_2Cl_2, to provide 46 mg (45%) of the furan esters as a 1.5:1 mixture of diastereomers.