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Iron Tricarbonyl Complexes in Oxidation Chemistry: Regio- and Stereoselective Oxyfunctionalization of Trienes by Singlet Oxygen and Dimethyldioxirane

Waldemar Adam* and Rosemarie M. Schuhmann

Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany

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The versatility of the iron tricarbonyl fragment as protecting group in the oxyfunctionalization of trienes has been examined. The photooxygenation of the unsaturated iron complexes **1**−**3** at low temperatures (−80 °C) afforded after Ph$_3$P reduction the allylic alcohols **4**, **4′**, **13**, and **22** in good to excellent yields. The persistence of the intermediary allylic hydroperoxides is reflected in the distance between the iron fragment and the reacting free double bond. Only the hydroperoxides derived from the homoallylic (most distant) substrate **1** are persistent enough to undergo the titanium tetraisopropoxide-catalyzed oxygen transfer to β-hydroxy epoxides. Epoxidation of the complexes **1** and **2a** with dimethyldioxirane could be optimized in boiling acetone to suppress oxidative destruction of the iron tricarbonyl ligand. The deprotection of the organic ligand with cerium(IV) ammonium nitrate (CAN) enables the convenient preparation of multiply functionalized cyclohexadienes. In contrast to these regio- and stereoselectively controlled transformations, the corresponding unprotected trienes **10** and **19a** react with singlet oxygen and dioxirane at all double bonds without any particular preference.

Introduction

Oxyfunctionalizations belong to the most important transformations in preparative organic chemistry for the synthesis of highly reactive building blocks. Among the recent catalytic oxidations of great synthetic value must be mentioned the enantioselective Sharpless epoxidation of allylic alcohols[1] and Kagan's modification for the sulfoxidation of alkenyl sulfides,[2] the Sharpless enantioselective *cis*-dihydroxylation of alkenes,[3] the enantioselective epoxidation of olefins with Jacobsen's catalyst,[4] and the oxidation of alkenes, arenes, and sulfides by Herrmann's system (methyltrioxorhenium/hydrogen peroxide).[5] On the photochemical front, molecular oxygen in sensitized oxygenation—singlet oxygen ($^{1}O_2$)—serves as a highly versatile oxidant for the functionalization of olefins. Allylic hydroperoxides, obtained through the ene process (Schenk reaction), and endoperoxides and 1,2-dioxetanes, produced by [4 + 2] and [2 + 2] cycloadditions, represent common reaction products.[6] Photooxygenation in the presence of Ti(OiPr)$_4$ or VO(acac)$_2$ enables a convenient direct access to epoxy alcohols by oxygen transfer of the intermediary allylic hydroperoxides.[7] Whereas such photooxygenations have become a standard tool for the oxyfunctionalization of olefins in organic chemistry, only little is known about the reaction of $^{1}O_2$ with organometallic compounds.

In contrast to singlet oxygen, dimethyldioxirane[8] (DMD), which is a powerful but selective reagent, plays an important role for oxyfunctionalizations in the ligand sphere of transition metal complexes. In this connection, examples are now known for all its three reaction modes, namely epoxidations,[9] heteroatom oxidation,[10] and X−H insertions.[11]

The regio- and stereoselective oxyfunctionalization of trienes with 1,3-dienic units by singlet oxygen and DMD represents a synthetic challenge due to the numerous directions of attack for the various reaction modes. For this purpose, we have examined the versatility of the iron tricarbonyl fragment for the protection of a cyclic 1,3-diene moiety in the substrate, a useful methodology which has been already well-established in preparative organic chemistry.[12] Herein we report on the unprecedented selective oxidation of iron tricarbonyl-protected, multiply unsaturated olefins, which enables the ready access to 1,3-cyclohexadienes with epoxy, allylic hydroxy,

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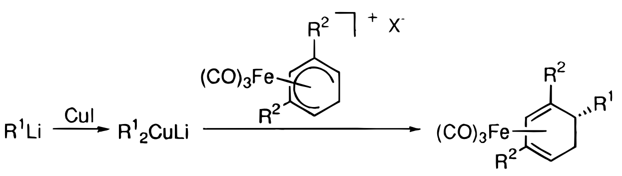
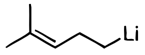
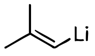
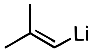
Scheme 1



R^1Li	R^2	X^-	product	yield (%)
	H	BF_4^-	**1**	85
	H	BF_4^-	**2a**	84
	Me	PF_6^-	**2b**	25

and *β*-hydroxy epoxy side chains. These oxyfunctionalized products represent useful building blocks for preparative purposes due to their varied functionalities and are not easily available by other means.[13]

Results and Discussion

The alkenyl-substituted, hitherto unknown iron tricarbonyl complexes **1** and **2** were synthesized analogous to Pearson's procedure[14] in yields up to 85% by addition of alkenyl cuprates, derived from the corresponding alkenyllithium compounds, to tricarbonyl(1−5-*η*-cyclohexadienyl)iron cations (Scheme 1).

Direct reaction of the alkenyllithium compounds[15] with the cations gave only about half of the yields reached with the cuprates. The known vinylic complex **3** (for its structure see Scheme 4) was synthesized according to the literature procedure.[16]

The iron tricarbonyl complexes **1**−**3** were oxyfunctionalized in moderate to high yields with singlet oxygen. In the case of derivatives **1** and **2a**, the photooxygenation was also conducted in the presence of titanium tetraisopropoxide.[7] In addition, both compounds were epoxidized with dimethyldioxirane as acetone solution.[17] The reaction progress was monitored by TLC and in the latter case complete dioxirane consumption was assessed by the peroxide test (KI in HOAc). Iron-derived paramagnetic impurities prevented the acquisition of NMR spectra directly on the crude product mixture and, therefore, silica gel chromatography was necessary to remove such disturbing materials. The oxyfunctionalizations were optimized with respect to temperature, reaction time, and amount of oxidant. Since the results depend on the location of the iron tricarbonyl moiety relative to the double bond to be oxidized, each substrate shall be discussed individually.

In general, the highest yields in the photooxygenation of the iron tricarbonyl-protected olefins were obtained at low temperatures due to the instability of the resulting hydroperoxides toward thermal decomposition. Therefore, before workup, the allylic hydroperoxides were reduced with triphenylphosphine immediately after photooxygenation. A control experiment assured that the iron tricarbonyl complexes themselves were stable toward hydroperoxides. Thus, the complex **1** and **3** persisted even for two weeks on exposure to *tert*-butyl hydroperoxide at −20 °C. A decrease in the temperature of the photooxygenation from −20 to −80 °C resulted in a ca. 2.5-fold higher yield of the alcohols after reduction; however, no oxidized product could be observed at 0 °C. At temperatures between −20 and −40 °C, the decomposition could be minimized, especially when ca. 25 mol % 2,6-di-*tert*-butyl-4-methylphenol was added as radical scavenger, which indicates that radical chain processes become important as side reactions at elevated temperatures. The disadvantage of using such phenolic scavengers is the difficulty of separating them from the desired oxyfunctionalized iron tricarbonyl products.

The photooxygenation results for iron complex **1** are displayed in Scheme 2. The two regioisomeric alcohols **4** and **4′** were isolated in 89% yield, for which the diastereomeric ratio was 54:46. The alcohol **4** was obtained as a 50:50 mixture of two diastereomers. In the presence of 24 mol % of titanium tetraisopropoxide[7] and under strictly anhydrous conditions, the photooxygenation at −10 °C afforded the two regioisomeric epoxy alcohols **6** and **6′** in 44% total yield. Besides, small amounts (ca. 8%) of the regioisomeric alcohols **4** and **4′** were formed by $Ti(OiPr)_4$ reduction as a side reaction.

The photooxygenation of the iron complex **2a** afforded after Ph_3P reduction the alcohol **13a** (Scheme 3) in 83% yield as a 57:43 diastereomeric mixture, with traces of the enone **14a** presumably by loss of water from the intermediary hydroperoxide. For characterization purposes, the enone **14a** was independently prepared by oxidation of the allylic alcohol **13a** with chromium trioxide in analogy to the literature procedure[18] (Scheme 3).

The intermediary hydroperoxide of the photooxygenation of **2a** was even more labile than that derived from

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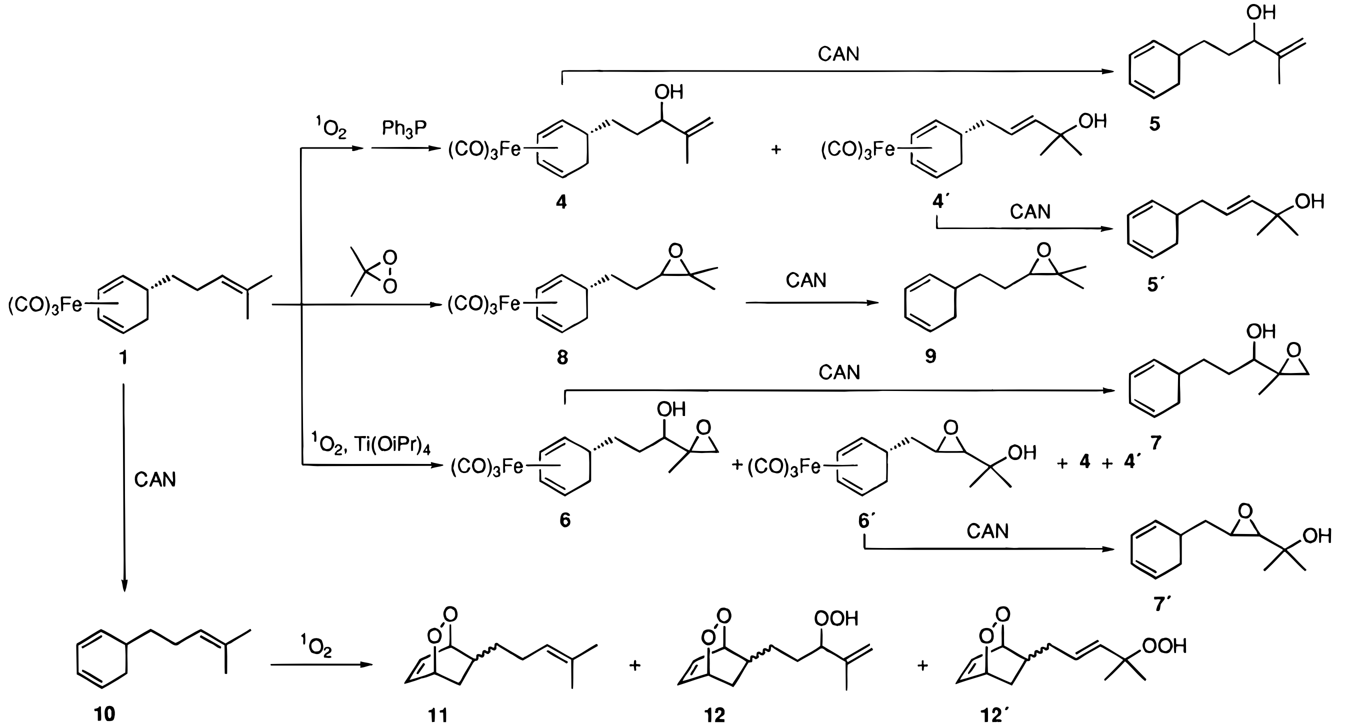
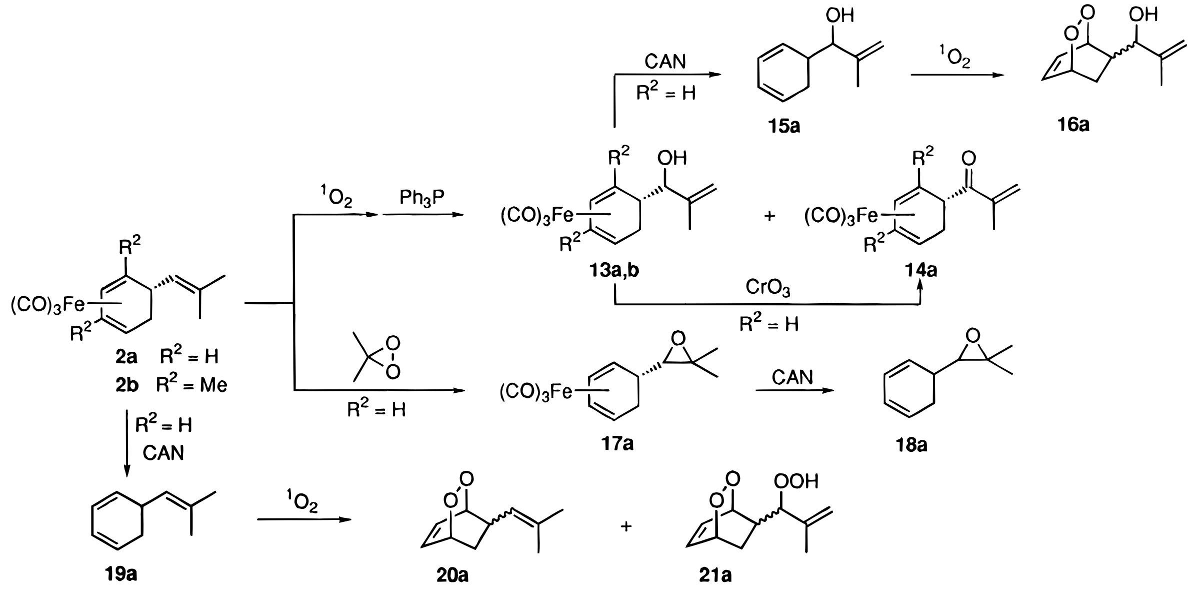
Scheme 2



complex **1**. An attempt to isolate the hydroperoxide by low-temperature silica gel chromatography failed and a 91:9 mixture of the allylic alcohol **13a** and its enone **14a** was obtained in only 22% yield. Presumably these minor products derive from iron-catalyzed decomposition of the labile allylic hydroperoxide. Consequently, an attempted oxygen transfer by titanium tetraisopropoxide to the corresponding epoxy alcohol directly during the photooxygenation failed, since temperatures of at least −10 °C are necessary. The only oxidation products obtained were **13a** and **14a** in merely 15% yield.

Scheme 3



The photooxygenation of the methyl-substituted iron complex **2b** afforded the allylic alcohol **13b** (63%) as a 69:31 mixture of diastereomers (Scheme 3). The less reactive iron complex **3** (Scheme 4), in which the free double bond is in conjugation with the complexed 1,3-dienic unit, resulted in the alcohol **22** (10%) in a diastereomeric ratio of 64:36 and the aldehyde **23** (6%). The latter is presumably the Hock cleavage product of the intermediary allylic hydroperoxide.[19] An attempted independent synthesis of the aldehyde **23** by ozonolysis of iron complex **3** led to complete oxidative destruction of the substrate.

When the photooxygenation results of the iron tricarbonyl complexes **1**, **2a**, and **3** are compared, it is conspicuous that the yields dramatically drop from 89% for the homoallylic derivative **1** (Scheme 2), 83% for the vinyl case **2a** (Scheme 3), to merely 16% for that of **3** (Scheme 4). In these three substrates the distance between the

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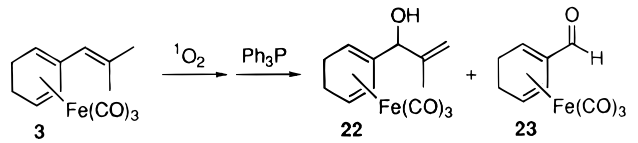
Scheme 4



resulting intermediary hydroperoxy functionality and the iron tricarbonyl functionalities decreases in the mentioned order, which exerts profound effects in the persistance of the intermediary hydroperoxides formed in the photooxygenation. For example, for the substrate **1** with the homoallylic sidechain (Scheme 2), the resulting hydroperoxides are persistent enough at −10 °C to undergo the titanium tetraisopropoxide-catalyzed oxygen transfer to the epoxy alcohols **6** and **6′**. In contrast, the hydroperoxide from the vinyl substrate **2a** (Scheme 3) decomposes on warming already below −10 °C, the temperature which is essential for the epoxy-hydroxylation. Nevertheless, immediate Ph_3P reduction at low temperatures (−80 °C) enables the isolation of alcohol **13a** in high yield. Similar results were obtained for the dimethyl derivate **2b** (Scheme 3). Even more labile is the hydroperoxide derived from the regioisomeric iron complex **3**, for which the hydroperoxy functionality is most proximate to the iron tricarbonyl-protected 1,3-diene moiety (Scheme 4). Presumably, intramolecular redox reactions between the hydroperoxy group and the neighboring metal center results in decomposition, as witnessed by the large amounts of undefined iron-containing material.

The iron tricarbonyl complexes **2b** and **3** were chosen to explore diastereoselectivity of the ene oxyfunctionalization. In the derivative **2b**, the methyl group in the 4-position of the cyclohexadiene ring (Scheme 3) should hinder rotation of the vinylic side chain and, thus, help to direct the incoming singlet oxygen on steric grounds. Unfortunately, the observed diastereoselectivity of 69:31 was only moderate. Despite the fact that iron tricarbonyl-mediated stereochemical directing effects are well established in literature,[20] the iron tricarbonyl fragment in substrate **3** (Scheme 4) does not direct the incoming singlet oxygen opposite to the iron tricarbonyl fragment for a stereoselective ene reaction.

Problematic in the epoxidation of iron tricarbonyl-protected olefins with DMD is the fact that DMD decomposes these iron complexes similar to those of chromium,[21] by direct oxidation of the iron atom or the CO ligands in both the starting materials and products. A control experiment with the iron tricarbonyl complex of cyclohexa-1,3-diene as model compound showed that the amount of decomposition ranged at −78 to 20 °C between 10−16% on treatment with 1 equiv of DMD. Consequently, since the epoxidation is favored at higher temperatures, the best compromise was to run the reaction in *boiling acetone* at ca. 56 °C with 3 equiv of the DMD oxidant. A higher excess of DMD was disadvantageous because of increased oxidative destruction of the epoxidized complex.

In this way, the DMD oxidation of iron complex **1** gave the epoxide **8** (Scheme 2) in 41% yield at 59% conversion as a 50:50 diastereomeric mixture. For the iron complex **2a**, the epoxide **17a** (Scheme 3) was obtained in 58% yield at a conversion of 60% as a 59:41 diastereomeric mixture. In contrast, the epoxidation with mCPBA under $NaHCO_3$-buffered conditions was unsuccessful. For example, with 1 equiv of peracid, after 20 h at 20 °C ca. 70% of starting iron complex **1** was reisolated, the rest was undefined iron-containing material. Similarly, direct epoxidation by Caroate[22] as well as the *in situ* method[23] with DMD also failed. Therefore, the reaction in boiling acetone with an excess (3 equiv) of isolated DMD is to date the best direct oxidative method to obtain the epoxides of iron tricarbonyl-containing unfunctionalized olefins. The only other oxidative method known in literature is the Sharpless epoxidation[24] of allylic and homoallylic alcohols with an iron tricarbonyl-protected dienic functionality. The base-catalyzed dehydrochlorination of chlorohydrins[25] serves as an nonoxidative method for the indirect epoxidation of iron tricarbonyl complexes with unfunctionalized double bonds.

The iron tricarbonyl complexes **1** and **2a** and their oxyfunctionalized derivatives (Scheme 2 and 3) were conveniently decomplexed with cerium(IV) ammonium nitrate[25,26] (CAN) mostly in high yields (up to 98%). Best results were obtained at a reaction time of one day under an argon gas atmosphere and 3 equiv of CAN at −5 °C. This temperature was chosen to prevent aromatization of the 1,3-diene moiety, which was observed for substrate **1** at 20 °C to an extent of 25%. In comparison, the use of trimethylamine *N*-oxide[27] for decomplexation led to a large amount of aromatization. Fortunately, in the decomplexation of the allylic alcohols **4**, **4′**, and **15** with CAN, no side reactions due to oxidation of the hydroxy to the keto functionality was observed. In contrast, the epoxy-substituted complexes **7**, **7′**, **9**, and **17a** had to be treated with CAN at 0 °C for only 0.5 h because the epoxide ring did not withstand longer exposure to these oxidative conditions.

For comparison with the oxyfunctionalization of the iron tricarbonyl-protected trienes, the decomplexed olefins **10** and **19a** were photooxygenated to test the advantages of the metal-assisted methodology. In most cases complex reaction mixtures were obtained for the decomplexed olefins (Schemes 2 and 3). Besides the expected endoperoxide **11** from olefin **10** (Scheme 2) and **20a** from **19a** (Scheme 3), also the hydroperoxides **12** and **12′** from **10** and **21a** from **19a** were observed. Attempts to control overoxidation by adjusting the photooxygenation time were of little effect since both $^1O_2$ reaction modes took place concurrently. As expected, the allylic alcohol **15a** was photooxygenated exclusively to the endoperoxide **16a** (65%) in a 64:36 *endo*:*exo* ratio (Scheme 3). This low diastereoselectivity lies in the normal range reported in literature[28] and signifies that for such chiral dienes the hydroxy functionality does not appreciably direct the incoming singlet oxygen dienophile.[29] Finally, the reaction of triene **19a** with DMD as well as with

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mCPBA (not shown in Scheme 3) resulted in a mixture of all possible epoxides without any regio- nor diastereoselectivity.

In summary, for the first time the oxidation of unsaturated tricarbonyliron complexes with singlet oxygen and DMD was shown to effect selective oxyfunctionalizations of the organic ligand. The results demonstrate the versatility of the iron tricarbonyl fragment as a protection group also for oxidation reactions. Since the oxyfunctionalizations and decomplexations of the iron tricarbonyl complexes **1**-**3** (Schemes 2−4) could be performed in good to excellent yields, the direct oxidation of organic ligands in organometallic complexes opens up interesting opportunities for preparative organic chemistry.

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Supporting Information Available: Experimental procedures, including synthesis and characterization data of all new compounds (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.

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