The Highly Selective Oxidation of a Tricarbonyliron Complex

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The tricarbonyliron complex **2a** underwent selective and diastereoselective oxidation with *tert*-butyl hydroperoxide at room temperature to provide, after decomplexation, the peroxyether **5** which, on reduction, yielded the corresponding secondary alcohol **7**.

With a view to carrying out iron carbonyl transfer reactions,[1] we prepared the diastereomeric carbonyliron complexes **2a** and **2b** from the cyclopentadiene **1**.[2,3] The outcome of this complexation depended strongly on the reaction conditions (see Scheme 1).[4] Whereas a low-temperature procedure employing $[Fe_2(CO)_9]$ gave, after 6 h, the β-complex **2b** as the main reaction product, the high-temperature version with $[Fe(CO)_5]$ gave rise predominantly to the α-complex **2a** (ratio 9:1) during the same reaction time. However, after heating for 20 h the α-complex **2a** was found to be the sole reaction product in 75% yield.

The assignment of these configurations was based on the observation of Philipsborn et al.[5] who have reported that the H_{syn} signals in the diastereomeric butadiene complexes **3a** and **3b** differ considerably, and that the neighbouring carbonyliron moiety causes a remarkable downfield shift of the *syn* proton in the β-complex **3b**.

Considering the downfield position of the angular methyl group in **2b** (δ = 1.61) compared to the more or less normal value in **2a** (δ = 0.96), we assigned the β-configuration to the former. This assignment was corroborated by decoupling experiments which confirmed that the axial protons H_A and H_B of the corresponding α-complex **2a** resonate at δ = 1.55 and δ = 2.58 (!), respectively, while the corresponding chemical shifts in diene **1** are δ = 1.08 and δ = 1.24.[6]

These observations indicate that the β-complex **2b** is the kinetically controlled reaction product, as observed for all cycloadditions with the corresponding diene.[7] The higher thermal stability of the α-complex **2a** leads, however, to complete conversion into this stereoisomer on heating at 140°C.

This particular stability may also serve as an explanation for the observed low reaction rates in oxidative decomplexation. Investigating this reaction with various oxidants we noticed that the carbonyliron complex seemed to be perfectly stable towards *tert*-butyl hydroperoxide in organic solvents. The typical yellow colour of the tricarbonyl complex was clearly visible even after one week at room temperature; concentration and flash-chromatography on silica gave, in more than 60% yield, an oily nonpolar compound of similar polarity to the starting material, but the NMR spectrum of this substance showed the complete absence of **2a** and indicated a *tert*-butyl ether (δ = 1.25[9]) as the reaction product. Whereas infrared bands at 2036 and 1964 cm^{-1} left no doubt about the presence of the carbonyliron moiety, the molecular ion of 468 mass units was completely consistent with a *tert*-butyl peroxyether.

The only hint about the constitution and configuration was also gained from NMR-spectroscopic data. The appearance of a narrow triplet at δ = 3.80 indicated an equatorial proton at a carbon atom carrying an oxygen substituent, which could be located either at C^6 or C^9; the remarkable steric hindrance to be expected for C^9 prompted us to assume structure **4**, in which the axial C^6 proton is replaced by a peroxyether. Supporting evidence for this assumption was obtained after decomplexation of **4** with a saturated solution of *N*-methylmorpholine *N*-oxide in acetone for two days at room temperature (Scheme 2).

In the NMR spectrum of the low-melting (m.p. = 77.9°C) crystalline material isolated from this reaction, a narrow triplet at δ = 4.95 again indicated an equatorial hydrogen, but in this case the multiplicity of the C^4 proton argued strongly in favour of a C^6 substituent. In all other dienes investigated so far[7] this proton had appeared as a narrow triplet, probably due to an allylic coupling to the axial proton at C^6. In contrast, one observes a sharp doublet for this proton with diene **5**, as would be expected for a compound with an axial substitutent at C^6. It was the well-known steric hindrance, however, usually observed with 1,3-diaxial substituents, that made us hesitate to rely on NMR-spectroscopic data alone. As crystals of the peroxyether **5** were available at this stage, the final proof for this provisional assignment was obtained from an X-ray structure determination and the result (Figure 1) proved the structure to be the one with 1,3-diaxial substituents on the ring system.

As expected, reduction by lithium aluminum hydride transformed this peroxide into the acid-labile secondary alcohol **7** which, on dissolution in chloroform or deuteriochloroform containing traces of hydrochloric acid, quickly led to the triene **6** even at room temperature. Interestingly, the chromatographic separation of our crude oxidation

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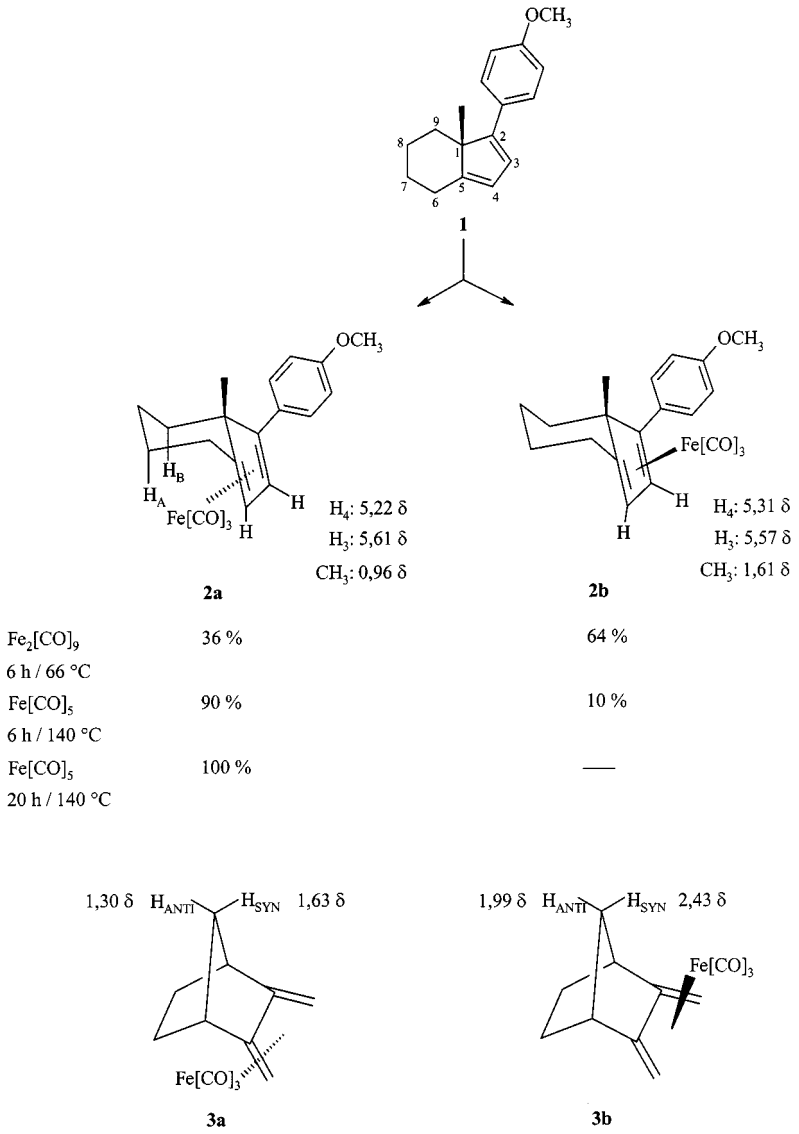


Scheme 1. Configuration assignment of iron carbonyl complexes

mixture gave several quite polar yellow fractions, which on decomplexation (see above) gave rise to a hydroxy compound identical (R_f value, IR and NMR spectra) to **7**, thus proving that this secondary alcohol is also formed directly in the oxidation process.

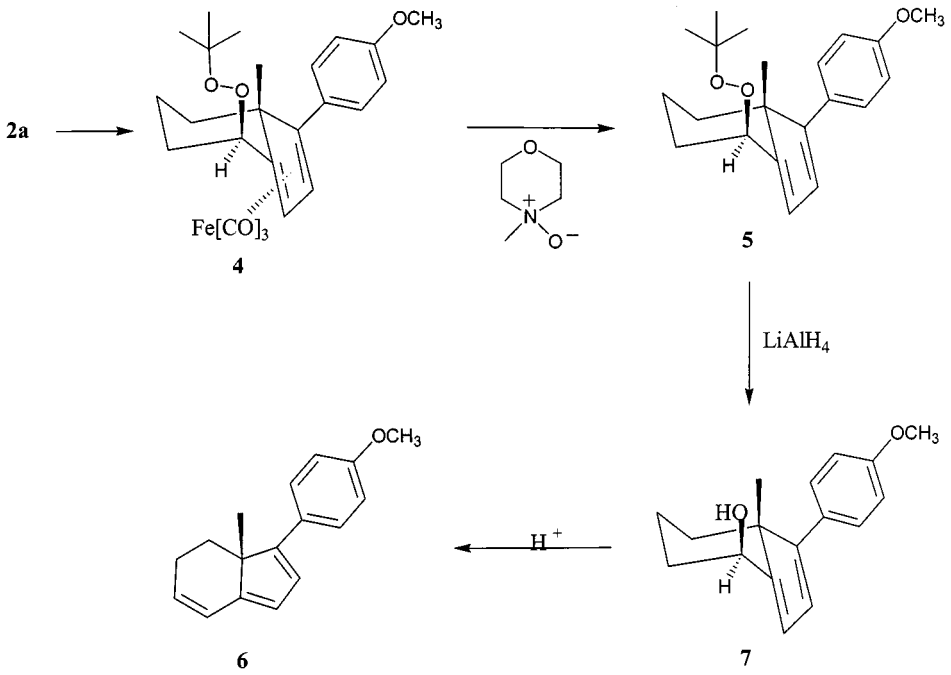
The high yield of this rather selective transformation, which falls in line with other diastereoselective transformations[8−12] in this field, together with the mild reaction conditions observed, indicate that this procedure may also be useful with other tricarbonyliron complexes.

Experimental Section

Melting points were determined with a Gallenkamp MPD 350 apparatus and are uncorrected. − NMR spectra were recorded with Bruker AM 400 or WP 200 instruments with Me_4Si or $CHCl_3$ (in $CDCl_3$) as internal standard. − IR spectra were recorded with Perkin−Elmer 580 and FT 1710 spectrometers. All reactions were monitored by thin-layer chromatography (TLC) carried out on DC-Alufolien Kieselgel $60F_{254}$ (Merck), with detection by UV light (λ = 254 nm) followed by treatment with cerium(IV) sulfate/phosphomolybdic acid and heating. Baker silica gel (particle size 0.03−0.06 mm) was used for flash column chromatography. Reagents were used as received.

Complex 2a: A solution of diene **1** (240 mg, 1 mmol) in 5 mL of dibutyl ether was treated with pentacarbonyliron (1.5 mL, 2.2 g, 11 mmol) and heated for 3 h at 140°C. Another 1.5 mL of pentacarbonyliron was added and the heating was continued for 6 h. The mixture was allowed to cool to room temperature, filtered through alox B and the solvent was evaporated. Subsequent flash chromatography on silica gel yielded 160 mg (75%) of an orange-red oil − ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 5.61 (d, J = 2 Hz, 1 H), 5.22 (d, J = 2 Hz, 1 H), 0.96 (s, 3 H) − ^{13}C NMR δ = 22.06, 22.16, 26.59, 32.23, 37.61, 55.15, 57.28, 79.35, 80.64, 82.90, 84.59, 113.82, 128.26, 130.19, 158.21, 213.92.

Peroxyether 4: Complex **2a** (380 mg, 1 mmol) was dissolved in a mixture of dichloromethane (35 mL) and *tert*-butyl hydroperoxide



Scheme 2. Chemical transformations of complex **4**

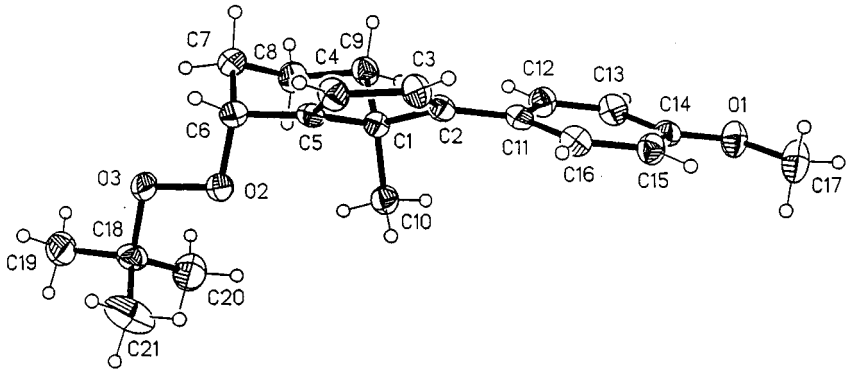


Figure 1. Structure of compound **5** in the crystal; ellipsoids indicate 50% probability levels; the O−O bond length is 1.4853(14) Å

(3.5 mL). This solution was left at room temperature for eight days and then the solvents were evaporated. The remaining red oil was purified by flash chromatography on silica (hexanes/diethyl ether 88:1) to give 280 mg (60%) of an orange oil. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.21 (d, J = 9 Hz, 2 H), 6.79 (d, J = 9 Hz, 2 H), 5.65 (AB-Q, J = 3 Hz, 2 H), 3.80 (m, 1 H), 3.79 (s, 3 H), 1.25 (s, 9 H), 1.01 (s, 3 H). − IR ($CHCl_3$): $\tilde{\nu}$ = 2976 cm^{-1} (s), 2928 (s), 2832 (s), 2036 (s), 1964 (s). − MS (EI, 140°C) *m/z* (%) = 468 (5), 440 (12), 384 (23), 278 (100), 238 (98).

For decomplexation this oil was treated with 5 mL of a saturated solution of *N*-methylmorpholine *N*-oxide overnight, diluted with water and extracted with ether. After concentration and filtration through silica a quantitative yield of peroxyether **5** was obtained; white crystals from hexane (m.p. 77.9°C). Standard $LiAlH_4$ reduction provided an 80% yield of the axial carbinol **7** (narrow triplet δ = 4.93) which proved to be identical to a more polar oxidation product from diene complex **2a**. This allylic carbinol proved to be acid-labile and was converted in quantitative yield into triene **6** on standing in dichloromethane at room temperature with a catalytic amount of *p*-toluenesulfonic acid.

X-Ray Structure Analysis of Compound 5: A colourless plate 0.7 × 0.3 × 0.04 mm was mounted on a glass fibre in inert oil. Data were measured at −100°C on a Siemens P4 diffractometer using monochromated Mo-K_α radiation; $2\theta_{max}$ = 50°, ω-scan mode. The structure was subjected to anisotropic full-matrix least-squares refinement using the program SHELXL-97. Hydrogen atoms were included using rigid methyl groups or a riding model. Crystal data: monoclinic, space group $P2_1/n$, a = 12.643(2), b = 5.9924(14), c = 24.793(5) Å, β = 95.409(12°), V = 1870.0 $Å^3$, Z = 4. Refinement proceeded to $wR2$ = 0.077, $R1$ = 0.037 for 222 parameters and all 3284 unique reflections, S = 0.84, max. Δρ = 0.13 e $Å^{-3}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication

no. CCDC-134885. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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