Pergamon

Tetrahedron Letters, Vol. 37, No. 4, pp. 423-424, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4039/96 $15.00 + 0.00

0040-4039(95)02203-1

Dihydroxylation/Glycol Cleavage of Tricarbonyl(triene)iron Complexes

William A. Donaldson* and Lewei Shang

Department of Chemistry, Marquette University, P.O. Box 1881, Milwaukee, WI 53201-1881

Abstract: (Polyene)Fe(CO)$_3$ complexes (**1**) are shown to be stable to a two-step osmylation/periodate cleavage sequence to produce (dienal)Fe(CO)$_3$ complexes (**2**). In contrast, ozonolysis of **1** has been reported to lead to destruction of the complex.

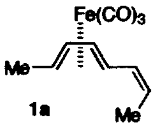
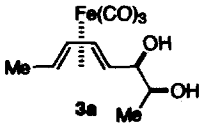
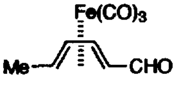
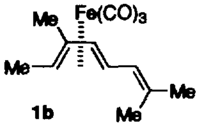
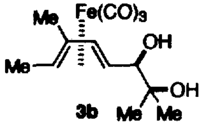
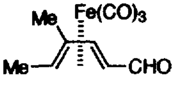
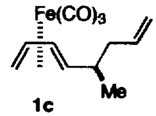
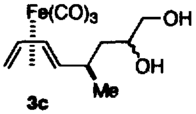
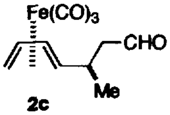
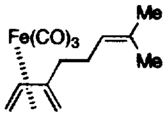
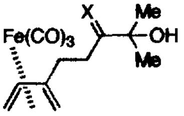
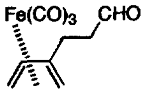
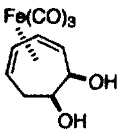
Coordination of a diene to a Fe(CO)$_3$ serves as an efficient method to protect the diene towards reduction and cycloaddition reactions. Furthermore, addition to unsaturated centers (C=O, C=N, or C=C) *adjacent* to the diene can occur in a diastereoselective fashion and this can be rendered into asymmetric stereoselectivity if the (diene)Fe(CO)$_3$ complex (**1**) is optically pure.[1] While the Fe(CO)$_3$ moiety is robust to a variety of reaction conditions, the oxidation of pendant functional groups (e.g. alcohol to carbonyl) is notoriously difficult due to competitive oxidative decomplexation.[2] The diene ligand in **1** may be liberated by a variety of oxidative conditions, i.e. ceric ammonium nitrate in methanol,[2,3] alkaline hydrogen peroxide,[4] peracid,[4] or ozonolysis.[4] In fact, the destruction of (diene)Fe(CO)$_3$ complexes by ozonolysis has been used as a "chemical purification" method for (trimethylenemethane)Fe(CO)$_3$ complexes contaminated with chromatographically inseparable triene complexes **1**.[5] We here report that the (diene)Fe(CO)$_3$ group survives the alternative two-step dihydroxylation/glycol cleavage sequence.

The stoichiometric osmylation of (diene)Fe(CO)$_3$ complexes with pendant olefins has been previously reported.[6] In this fashion, osmylation of trienes **1a**, **1b** and **1e** gave the corresponding glycols **3a**, **3b** and **3e** (Table 1). Catalytic osmylation (5% OsO$_4$, tBuOOH)[7] of **1c** gave **3c** as a mixture of diastereomers (ca. 1:1), while under the similar conditions **1d** gave **3d** (43%, 1:1 mixture of diastereomers) along with keto-alcohol **4** (18%) which could be separated by column chromatography. Reduction of **4** (NaBH$_4$/MeOH) gave **3d** (75%).

Treatment of **3a** with NaIO$_4$ in THF/H$_2$O/23°C gave the known dienal **2a** (61%) over a period of 18h. Cleavage with Pb(OAc)$_4$/pyr was considerably more rapid (10 min), however lower yields were obtained due to competitive destruction of the Fe(CO)$_3$ moiety. In a similar fashion, treatment of the glycols **3b**-**3d** with NaIO$_4$ gave the corresponding aldehydes **2b**-**d** in moderate yields (Table 1). The presence of the aldehyde functionality in complexes **2** was evident from IR and NMR spectral analysis. In contrast, treatment of **3e** under the same reaction conditions (23°C) gave only recovered **3e** while reaction with NaIO$_4$ at reflux or with Pb(OAc)$_4$/pyr led only to oxidative destruction of the starting material. The lack of reactivity of **3e** toward NaIO$_4$ might be attributed to restricted conformational mobility in the cyclic diol.

The following is a typical procedure: A solution of **3b**[6] (0.15 g, 0.48 mmol) and NaIO$_4$ (0.22g, 1.03 mmol) in THF/H$_2$O (10 mL/5 mL) was stirred at rt for 4 h. Additional NaIO$_4$ (0.63 g, 0.61 mmol) was added and the reaction mixture was stirred until the disappearance of **3b** was complete (TLC monitoring, 18 h). The reaction mixture was poured into water (20 mL), extracted with ether (2 x 50 mL), dried (MgSO$_4$) and concentrated. Chromatographic purification gave **2b** as orange needles (60 mg, 50%).

TABLE 1. Dihydroxylation/Glycol Cleavage of (triene)Fe(CO)$_3$ Complexes (1)

(triene)Fe(CO)$_3$		glycol product		cleavage product
 **1a**	OsO_4 (1.2 eq) tBuOOH (2 eq) Et_4NOAc (0.3 eq) acetone/3 h (48%)	 **3a**	$NaIO_4$ (1.4 eq) THF/H_2O/18 h (61%), or $Pb(OAc)_4$ (1.3 eq) pyr/10 min (37%)	 **2a**
 **1b**	OsO_4 (1.3 eq) pyr/6.5 h (89%)	 **3b**	$NaIO_4$ (3.4 eq) THF/H_2O/22 h (50%)	 **2b**
 **1c**	OsO_4 (0.05 eq) tBuOOH (2.4 eq) Et_4NOAc (0.27 eq) acetone/5 h (31%)	 **3c**	$NaIO_4$ (2.2 eq) THF/H_2O/18 h (49%)	 **2c**
 **1d**	OsO_4 (0.05 eq) tBuOOH (2.2 eq) Et_4NOAc (0.27 eq) acetone/2 h $NaBH_4$ (75%)	 **3d**, X = H, OH (43%) **4**, X = O (18%)	$NaIO_4$ (2.1 eq) THF/H_2O/24 h (45%)	 **2d**
 **1e**	OsO_4 (0.9 eq) pyr/THF/48 h (26-43%)	 **3e**	$NaIO_4$ (2.1 eq) THF/H_2O/rt/24 h	no reaction
			$NaIO_4$ (2.1 eq) THF/H_2O/reflux/24 h	destruction of **3e**
			$Pb(OAc)_4$ (1.2 eq) pyr/30 mn	destruction of **3e**

Acknowledgment. Financial support for this work was provided by the National Institutes of Health (GM-42641). We thank Mr. Bireshwar Dasgupta for the preparation of **3a**.

REFERENCES AND NOTES

1) Donaldson, W.A. in "Comprehensive Organometallic Chemistry II", Abel, E.W.; Stone, F.G.A.; Wilkinson, G. (eds.), Elsevier Science Ltd., Oxford, 1995, Vol. 11, Chpt 6.2.
2) Nunn, K.; Mosset, P.; Grée, R.; Saalfrank, R. W. *J. Org. Chem.* **1992**, *57*, 3359-64; Tao, C.; Donaldson, W. *J. Org. Chem.* **1993**, *58*, 2134-43.
3) Franck-Neumann, M.; Colson, J.-P. *Synlett* **1991**, 891-4.
4) Franck-Neumann, M., in: *Organometallics in Organic Synthesis*, de Meijere, A.; tom Dieck, H. (eds.), Springer-Verlag, Berlin, 1987, pp. 247-64.
5) Franck-Neumann, M.; Kastler, A. *Synlett* **1995**, 61-63.
6) Johnson, B.F.; Lewis, J.; Parker, D.G.; Postle, S.R. *J. Chem. Soc., Dalton Trans.* **1977**, 794; Gigou, A.; Beaucourt, J.P.; Lellouche, J.P.; Grée, R. *Tetrahedron Lett.* **1991**, *32*, 635-8.
7) Pearson, A.J.; Srinivasan, K. *J. Org. Chem.* **1992**, *57*, 3965-73.

(*Received in USA* 25 *October* 1995; *accepted* 13 *November* 1995)