Tetrahedron Vol. 48, No. 11, pp. 2013-2024, 1992
Printed in Great Britain

0040-4020/92 $3.00+.00

STEREOCHEMICAL ASPECTS OF CATALYTIC SILOXYMETHYLATION OF VARIOUS OXYGEN-CONTAINING COMPOUNDS WITH HYDROSILANES AND CARBON MONOXIDE IN THE PRESENCE OF DICOBALT OCTACARBONYL

Naoto Chatani, Toshiaki Murai, Toshihiro Ikeda, Takahiro Sano, Yasuteru Kajikawa, Kouichi Ohe, and Shinji Murai*

Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Suita, Osaka 565, JAPAN

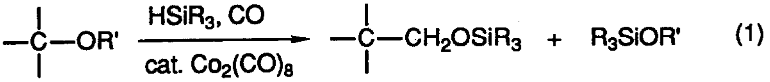
(*Received in USA* 27 *October* 1991)

Key words: catalytic reaction, stereochemistry, dicobalt octacarbonyl; carbon monoxide; hydrosilane

Abstract: Siloxymethylation of oxygen-containing compounds by a new catalytic reaction, $HSiR_3/CO/Co_2(CO)_8$, is described with emphasis laid on stereoselectivity. In the catalytic reaction, the carbon-oxygen bond in the substrates is cleaved and displaced by a trialkylsiloxymethyl group. The siloxymethylation takes place with inversion, racemization, or retention at the reaction sites, depending on the structure of the substrates.

Introduction

In the course of our studies on the $HSiR_3/CO/Co_2(CO)_8$ catalytic reaction,[1] we found that incorporation of carbon monoxide into a variety of oxygen-containing compounds took place under exceptionally mild reaction conditions (ambient temperature and atmospheric pressure of CO). The overall process of the catalytic reaction is introduction of a trialkylsiloxymethyl group into the carbon atom at the site where carbon-oxygen bond is cleaved (eq 1). For the catalytic siloxymethylation to take place at mild reaction conditions, the substrate must be reactive enough toward the key catalytic species $R_3SiCo(CO)_4$[1] at room temperature.

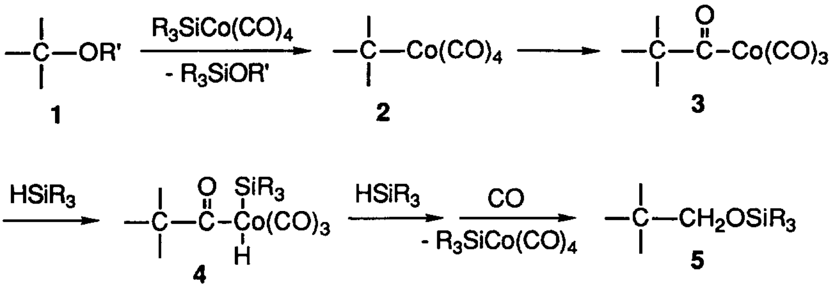


$$-\overset{|}{\underset{|}{C}}-OR' \xrightarrow[\text{cat. } Co_2(CO)_8]{HSiR_3,\ CO} -\overset{|}{\underset{|}{C}}-CH_2OSiR_3 + R_3SiOR' \qquad (1)$$

We have already found that oxiranes,[2] oxetanes,[3] five-membered cyclic ethers,[4] β-lactones,[5] glycosyl acetates,[6] acetals,[7] benzylic acetates,[8] and orthoesters[9] are sufficiently reactive to participate in this reaction. In this paper we wish to describe and discuss the stereochemical course of the catalytic siloxymethylation with representative examples. The stereochemistry of the carbon-carbon bond forming reaction has been found to vary from inversion to racemization, with retention in a special case, depending on the structure of the oxygen-containing compounds used as the substrates.

Results and Discussion

The catalytic siloxymethylation (eq 1) is believed to proceed as outlined in Scheme I. The reaction of oxygen-containing compounds **1** with the key catalyst species $R_3SiCo(CO)_4$[1,10] results in the formation of a carbon-cobalt bond in **2**. The formation of a carbon-transition metal bond is essential for incorporation of carbon monoxide. Migratory insertion of CO in **2** to give **3** followed by oxidative addition of a hydrosilane would afford **4**. Subsequent steps from **4** to the product **5** are still mechanistically not clear. The stereochemical relationship between the starting material **1** and the final product **5** must be determined in the process from **1** to **2** since the migratory insertion of CO in alkylmetal complexes like **2** to acylmetal complexes like **3** has been known to proceed with retention of configuration at the migrating carbon atom.[11]



Scheme I. Simplified Mechanism of the Catalytic Siloxymethylation