Stereo-divergent C–C Bond Formation on Arene–Chromium Template: Endo-Selective Allylation by Hosomi–Sakurai Reaction

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Introduction

In arene–tricarbonylchromium complexes, excellent diastereocontrol at benzylic or homobenzylic sites can be achieved since the Cr(CO)3 group effectively blocks one face of the molecule and prevents approach of reagents from this direction.1 This feature has been widely utilized in designing useful synthetic strategies.2 Suitable structured substrates allow almost total diastereoselectivity; i.e., the allyl group was delivered from the exo face, i.e., the face opposite to the metal; endo-selective reactions are particularly rare.3e Herein we wish to report a completely endo-selective Hosomi–Sakurai allylation4 on the 2-arylidenetetralone–Cr(CO)3 complex. The corresponding exo-allyd was obtained by an alternative sequence of reactions. In addition to displaying an unusual stereochemical preference, the TiCl4-catalyzed allylation reaction provides a prima facie evidence of out-of-plane coordination of titanium to the ketone dictating steric course of the reaction.

Results and Discussion

The enones 1a,b were prepared by condensation of appropriate aldehydes with 1-tetralone–Cr(CO)3 complex as reported earlier.3a The trans-stereochemistry was established from the low-field olefinic proton at 7.8 ppm, the proton being deshielded by the anisotropy of the carbonyl group.6

Allylmagnesium bromide readily added to the complexed enone 1a in THF to furnish the allylic alcohol 2a as a single diastereomer (Scheme 1). Since addition of Grignard reagents is known to occur with complete exo selectivity7 in these substrates, the orientation of the hydroxy group has been deduced as endo in the product. Treatment of 2a with potassium hydride and a catalytic amount of 18-crown-6 in ether at room temperature resulted in smooth anionic oxy-Cope rearrangement8 to produce the ketone 3a as a single diastereoisomer, in nearly quantitative yield. Equilibration of 3a with DBU/CH2Cl2 yielded a minor isomer 3a′ (3a:3a′ = 85:15), which must be epimeric at the carbon adjacent to the ketone. The relative stereochemistry of complex 3a was conclusively established from the crystal structure. The structure revealed that the complex 3a had the expected stereochemistry; i.e., the allyl group was delivered from the exo face of the molecule during the anionic oxy-Cope rearrangement from an exo-allyl carbinol. The same results were obtained with complex 1b.

When the complex 1a (or 1b) was treated with allyltrimethylsilane and TiCl4 at −78 °C, the product 4a (or 4b) was obtained as a single diastereomer (Scheme 2). The structural features of the 1,4-adduct were readily deduced from its 1H NMR spectral characteristics. A minor isomer 4a′ was obtained from equilibration of the complex 4a (4a′:4a = 89:11). The 1H NMR spectrum of complex 4a was similar to but not identical with that of complex 4a′, indicating isomerism (epimeric at C-2).

The 1H NMR spectra of all these stereoisomers derived from the same precursor via different routes were different. Since the isomers 3a and 3a′ are epimeric at C-2 of tetralone—so are 4a and 4a′—the two sets must differ in the relative configuration at the site of allyl addition. The crystal structure of complex 4a confirmed this fact. It was evident that the allyl group was appended from the endo-face of the substrate, contrary to normal expectation. These structures also established that proton quench of the enolate resulting from both the Hosomi–Sakurai allylation as well as the anionic oxy-Cope rearrangement took place from the exo face preferentially (3a and 4a are major isomers after equilibration).

The origin of this unusual stereochemical preference in the Hosomi–Sakurai reaction is probably inherent in the mode of binding of the Lewis acidic metal to the carbonyl group.9 The first step of this reaction is complexation of the strong Lewis acid TiCl4 to the enone carbonyl, which should normally take place from the direction of the nonbonded electron pair on oxygen.10 In this case, the chromium-complexed aromatic ring and the enone functionality are coplanar and the array of sp2 carbons form part of a rigid bicyclic system. The oxygen


atom is also sp²-hybridized, and hence, the two non-bonded electron pairs on oxygen are coplanar with these carbons. In this situation, the peri proton of the aromatic ring as well as the olefinic proton can shield the oxygen electron pairs from approach of the Lewis acid from either end (Figure 1).

Out-of-plane coordination of titanium with the CO π-bond has been structurally characterized.  However, such coordination has sometimes been described as η₁, in reality, the Ti–O distance is evidently shorter than the Ti–C bond. One should more appropriately consider a bond between Ti and a sp³ oxygen, which in turn implies that the carbonyl center is rendered cationic and thus the enone function is activated for reaction with allyltrimethylsilane.  It is then likely that TiCl₄ (which may exist as aggregates) would occupy the exo face (away from the tricarbonylchromium) and force the allyltrimethylsilane to approach from the endo face of the molecule at C-3.

Summary

In summary, we have presented a rare example of endo-selectivity in arene–chromium chemistry, as observed in conjugate allylation of 2-aryliden-1-tetralone Cr(CO)₃ complex using the Hosomi–Sakurai reaction. Normal exo-selectivity is observed for a similar functionalization via a Grignard–anionic oxy-Cope sequence. Such stereodivergence adds greater flexibility to the design of stereoselective strategies using arene–chromium complexes. The origin of this unusual stereochemical preference may be traced to an out-of-plane coordination of titanium with the carbonyl oxygen. We are currently exploring this theme in the context of π-facial selectivity in a number of varied structures, especially conformationally flexible acyclic substrates.

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Supporting Information Available: Experimental details and full characterization of complexes 1a, 2a, 3a, 4a, and 4a, and ORTEP diagrams for complexes 3a and 4a, and ¹H NMR spectral comparisons of 3a, 3a', 4a, and 4a' (6 pages).