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Preliminary communication

(η^6-Arene)chromium complexes in organic synthesis: [2,3]-Wittig rearrangement of (benzyl crotyl ether)-chromium complexes

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Abstract

The [2,3]-Wittig sigmatropic rearrangement of (benzyl (*E*)-crotyl ether)chromium complexes is shown to give a *syn* stereoselection which is different from the *anti* selection reported for the corresponding chromium-free compounds.

The [2,3]-Wittig sigmatropic rearrangement has become an efficient method for acyclic stereocontrol [1]. It has already been reported [2] that the Wittig rearrangement of benzyl (*Z*)-crotyl ether provides extremely high *syn* stereoselection, whereas the corresponding (*E*)-substrate gave poor stereoselectivity. The mechanism of stereoselection in the [2,3]-Wittig rearrangement has been rationalized in terms of the pseudo 1,3-diaxial interaction and the gauche interaction in the enveloped five-membered transition state [1,3]. Since the extent of stereoselectivity is influenced by the steric bulkiness of substituents, the modification of aromatic ring to a sterically bulkier group, e.g., by a temporary chromium complexation, is of interest in the synthetic application and the mechanistic study of the [2,3]-Wittig rearrangement. Here we report on the high *syn* diastereoselection, and the asymmetric induction in the Wittig rearrangement [4*], by (benzyl (*E*)-crotyl ether)chromium complexes.

Treatment of (benzyl (*E*)-crotyl ether)$Cr(CO)_3$ (**1a**) with lithium diisopropylamide (LDA) in THF at $-78°C$ for 7 h afforded a diastereomeric mixture of *syn*-**2a** and *anti*-**2b** in a ratio of 95/5 after demetalation by exposure to sunlight. The high *syn* selectivity of (*E*)-substrate is in contrast to the results for the chromium-free parent compound [2], and can be explained as follows. The coordination of sterically bulky $Cr(CO)_3$ would greatly enhance the gauche interaction between

* Reference number with asterisk indicates a note in the list of references.

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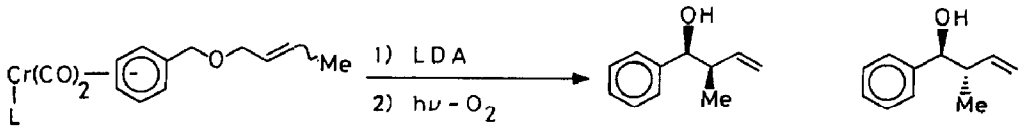
Table 1

[2,3]-Wittig rearrangement of chromium complex 1

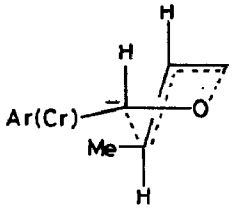


1 2 a 2 b

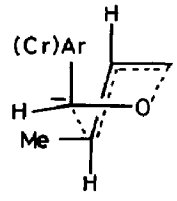
Entry	Substrate	Geometry (purity)	2a/2b	Yield (%) [a]
1	**1a**, L = CO	E (96%)	95/5 [b]	69
2	**1b**, L = PPh_3	E (96%)	88/12 [b]	95
3	**1c**, L = CO	Z (88%)	48/52 [b]	40

[a] A mixture of 1 mmol of complex **1** and 3 equiv. of LDA in THF (10 ml) was stirred at −78 °C for 7 h under argon. The rearranged chromium complex was dissolved in 10 ml of ether and the solution was exposed to sunlight until a yellow solution disappeared. [b] The ratio was determined by ^1H NMR (400 MHz).

Ar(Cr) and methyl groups in the transition state **A**, and, therefore, another transition state **B** having a pseudo axial substituent would favor rearrangement to *syn*-**2a**. Similarly, a bulkier substrate **1b** with one triphenylphosphine ligand rearranges smoothly to give *syn*-**2a** in good yield but with lower selectivity. On the other hand, the corresponding (*Z*)-crotyl complex **1c** gives a 1/1 diastereomeric mixture.

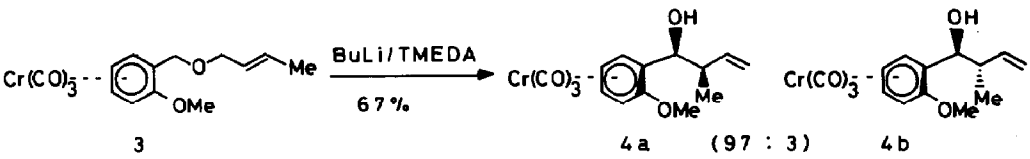


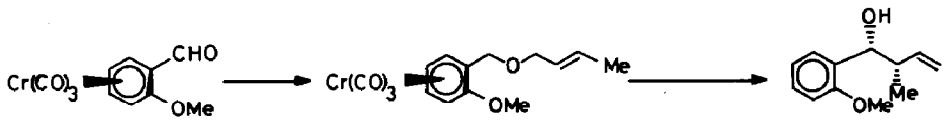
A



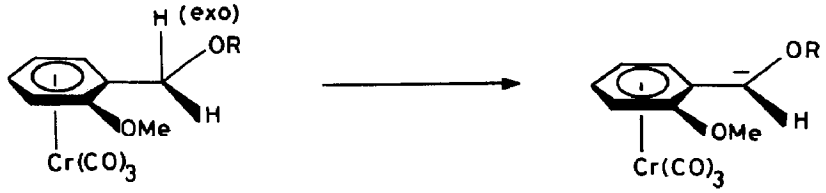
B

The [2,3]-Wittig rearrangement of (di-substituted arene)chromium complexes is also of interest in view of the stereochemistry of the rearranged chromium complexes which can exist in four diastereomeric *dl*-forms. The reaction of (*o*-methoxybenzyl-(*E*)-crotyl ether)$Cr(CO)_3$ (**3**) ($E > 99.3\%$) with n-BuLi in the presence of TMEDA at −78 °C gives two diastereomeric chromium complexes, *syn*-**4a** ($1R^*,2S^*$)-(ArR^*) [5*] and *anti*-**4b** ($1R^*,2R^*$)-(ArR^*) [5] in a ratio of 97/3 without the formation of the other two diastereomers. The formation of **4a** and **4b** can be explained in terms of an *exo* deprotonation [6] from sterically most favorable conformation **C**, in which the methoxyl group is oriented *anti* to the side chain-ether moiety, followed by an *exo* attack of the rearranging double bond on the benzylic carbanion of conformation **D**. Furthermore, the chromium complex **3** can be

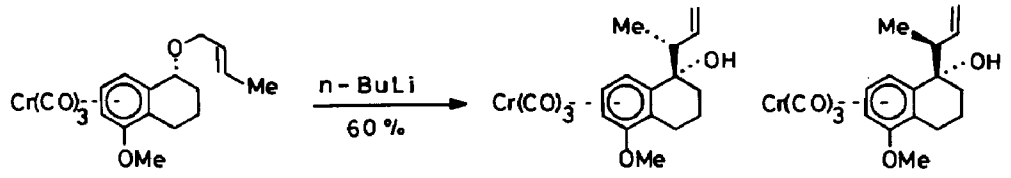




employed as a "template" for highly asymmetric induction in the Wittig rearrangement. The optically pure (−)-(*R*)-(*o*-methoxybenzaldehyde)$Cr(CO)_3$ [7], when reduced with $LiAlH_4$, gives the (+)-(*R*)-(*o*-methoxybenzyl alcohol)chromium complex, which is converted into the (*R*)-(*E*)-chromium complex **6** ($[\alpha]_D$ 165°, $CHCl_3$) by treatment with (*E*)-crotyl alcohol and $ZnCl_2$ [8]. The Wittig rearrangement of the complex **6** under the same conditions gives (1*R*,2*S*)-1-*o*-methoxyphenyl-2-methyl-3-buten-1-ol (**7**) ($[\alpha]_D$ 21°, $CHCl_3$, > 99%ee) after photo-oxidative demetalation.



A high *syn* selection is also evident in chromium complexes having an alkyl substituent at the benzylic position. For example, the *endo*-(1-(*E*)-crotyloxy-5-methoxytetraline)$Cr(CO)_3$ (**8**) was treated with n-BuLi to give predominantly *syn* rearranged chromium complex **9a**, the product ratio being in marked contrast to that obtained from the reaction [9] of (5-methoxy-1-tetralone)$Cr(CO)_3$ and crotylaluminum "ate" complex.



The highly stereoselective [2,3]-Wittig rearrangement in the arenechromium complexes possesses another advantage for acyclic stereocontrol, since the resulting benzylic alcohol can be substituted stereospecifically by suitable nucleophiles via

$Cr(CO)_3$-stabilized carbocations [10]. A study on further synthetic application to natural products is now in progress.

References

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