Chapter - 1: Stereoselective Synthesis using Arene Chromium Tricarbonyl Complexes - A Review

Arene chromium tricarbonyl complexes has been extensively used as a stereoface-directing group whereby considerable stereocontrol can be achieved in various organic reactions. In this review, significant results pertaining to this aspect of the arene-chromium chemistry have been discussed to serve as a background to the present work.

Chapter - 2: Conjugate Nucleophilic Addition to Enones Complexed with Tricarbonylchromium

In order to investigate the steric effect of chromium tricarbonyl at a site three carbon removed from the metal-complexed arene ring, Michael reactions on suitable benzylidene substrates were carried out with different nucleophiles. Aromatic aldehydes were condensed with 1-tetralone complexed with Cr(CO)₃ in ethanolic potassium hydroxide to provide the substrates (1a-d) in excellent yield. Conjugate addition of nitromethane (solvent) was carried out with KF (stoichiometric) and 18-Crown-6 (catalytic) at room temperature. A pair of diastereomeric products (2a-d and 3a-d) were obtained in good to very good yield in each case. These were separated by column chromatography and characterized.

\[ \text{Ar} \]

a : \text{C}_6\text{H}_5
b : p-\text{CH}_3-\text{C}_6\text{H}_4
c : p-\text{OCH}_3-\text{C}_6\text{H}_4
d : p-\text{NO}_2-\text{C}_6\text{H}_4

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It was established that the nucleophile added to the substrate with 100% stereospecificity from the face opposite to the metal. The epimers had arisen out of a keto-enol equilibrium at the centre adjacent to the carbonyl group. The relative configuration of the major isomer was confirmed by X-ray crystal structure analysis. It was shown that preferential protonation also occurred from the face opposite to the metal, as anticipated. The NMR peak assignments were carried out with COSY and HETCOR experiments. Conjugate addition of nitromethane on the acyclic substrates 4α-c occurred with modest selectivity. With dimethyl malonate as the nucleophile, a tricyclic product was obtained as single diastereomer. The structure of the compound was assigned as an enol lactone.

\[
\begin{align*}
\text{Ar} \quad 4\alpha-c \\
\text{O} \quad \text{OCH}_3 \\
\text{Cr(CO)}_3 \\
\text{Ar} \\
\text{CH}_2\text{NO}_2 \\
\text{O} \quad \text{OCH}_3 \\
\text{Cr(CO)}_3 \\
\end{align*}
\]

\[\text{Ar} \quad 5\alpha-c \]

\[
\begin{align*}
\text{Ar} \\
\text{a} : & \text{C}_6\text{H}_5 \\
\text{b} : & \text{p}-\text{CH}_3-\text{C}_6\text{H}_4 \\
\text{c} : & \text{p}-\text{OCH}_3-\text{C}_6\text{H}_4
\end{align*}
\]

\[
\begin{align*}
\text{Ar} \quad 6\alpha-b \\
\text{O} \quad \text{CO}_2\text{CH}_3 \\
\text{Cr(CO)}_3 \\
\text{Ar} \\
\text{a} : & \text{C}_6\text{H}_5 \\
\text{b} : & \text{p}-\text{CH}_3-\text{C}_6\text{H}_4
\end{align*}
\]
Chapter - 3: *Lewis Acid Mediated Conjugate Addition of Allylsilane and Allylstannane to Enones Complexed with Tricarbonylchromium*

TiCl₄-mediated conjugate addition of allyltrimethylsilane and allyltributylstannane to the tetralone-benzylidene complexes 1a-b yielded the products 7a-b as single diastereomer in very good yield. Titanium tetrachloride proved to be the most efficient Lewis acid for this reaction. The formation of a single diastereomer is probably the result of low-temperature kinetic quench of the titanium enolate. The low-temperature reaction proceeded with appreciable stereoselectivity (70:30) even on the acyclic substrate 4a-c to afford the products 8a-c in very good yield.

\[
\begin{align*}
\text{Cr(CO)}_3 & \quad \text{7a-b} \\
\text{Ar} & \\
\text{a: } & \text{C}_6\text{H}_5 \\
\text{b: } & \text{p-CH}_3\text{-C}_6\text{H}_4
\end{align*}
\]

\[
\begin{align*}
\text{Cr(CO)}_3 & \quad \text{8a-c} \\
\text{OCH}_3 & \\
\text{Ar} & \\
\text{a: } & \text{C}_6\text{H}_5 \\
\text{b: } & \text{p-CH}_3\text{-C}_6\text{H}_4 \\
\text{c: } & \text{p-OCH}_3\text{-C}_6\text{H}_4
\end{align*}
\]

Chapter - 4: *Cyclopropanation of the Enones Complexed with Tricarbonylchromium*

Cyclopropanation using sulfoxonium ylides can be viewed as a nucleophilic attack followed by intramolecular electrophilic cyclization. Using trimethylsulfoxonium iodide with 50% aq sodium hydroxide
solution in dichloromethane containing 2 mol% of tetrabutylammonium bromide the cyclopropanated products 9a-c were obtained from the substrates 1a-c, in very high yield as single diastereomer. Uncomplexed 2-benzylidene-1-tetralone did not undergo cyclopropanation under the same condition. The X-ray crystal structure of the compound 9a revealed that the cyclopropane was actually appended from the same face as that of the metal. Such reversal of stereoselectivity on arene-Cr(CO)₃ complexes is unprecedented. The steric course remained the same when the reaction was carried out in tetrahydrofuran with preformed ylide under homogeneous condition.

\[
\begin{align*}
\text{Cr(CO)}_3 & \\
\text{Ar} & \\
9a-c
\end{align*}
\]

\[a: \text{C}_6\text{H}_5 \]
\[b: p-\text{CH}_3-\text{C}_6\text{H}_4 \]
\[c: p-\text{OCH}_3-\text{C}_6\text{H}_4 \]
Chapter - 5: 3 + 2 Cycloaddition of Diazomethane to Enones Complexed with Tricarbonylchromium

Diazomethane reacts with enones to provide the 3 + 2 cycloaddition product. On treatment with an ethereal solution of diazomethane, the tricarbonylchromium complexes 1a-c afforded the diastereomeric cycloaddition products 10a-c and 11a-c, which were separated by chromatography and characterized by spectroscopy and elemental analyses. Pyrolysis in refluxing toluene cleanly afforded the enones 12a-c irrespective of the diastereomer used, and no cyclopropane was detected.

Note: The compound numbers incorporated in the Synopsis are different from those appearing in the Thesis.