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SHORT COMMUNICATION

Use of a Chromium Tricarbonyl Complex in a Diels–Alder Reaction: Improved Preparation of Angularly Trifluoromethyl-substituted Tetrahydrophenanthrone

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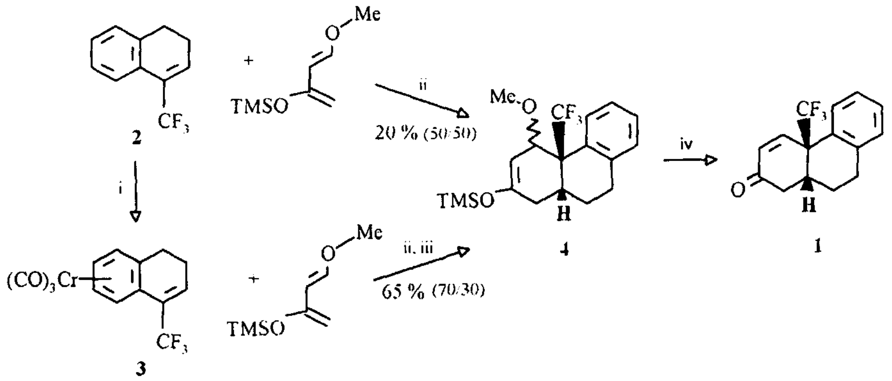
The tricarbonyl complex prepared from 1-trifluoromethyldihydronaphthalene and $Cr(CO)_3(NH_3)_3$ undergoes Diels–Alder cycloaddition under high-pressure conditions (15 kbar) to give after decomplexation by natural light and deprotection, the tetrahydrophenanthrone product in 65% yield. This new methodology allows the activation of unreactive styrenes in Diels–Alder cycloaddition.

Keywords: Arene chromium carbonyl complex, trifluoromethyl compounds, Diels–Alder cycloaddition, diterpenes

Cycloaddition reactions performed with ethylenic compounds which are not activated by a carbonyl substituent are often limited, because of their low reactivity. Catalysis by Lewis acid complexation is not possible, so another type of activation has to be considered. We took advantage of our investigations into cycloadditions performed on trifluoromethyl styrene derivatives[1-3] to assess the promoting effect of $n-6$ tricarbonyl chromium complexes. Chromium carbonyl complexes are widely used in various synthetic strategies,[4] both as activating ligands and as chiral auxiliaries. In cycloaddition reactions, they have been recently used to promote discrimination between the two faces of either or both reactants.[5-8] However, their activating effect on dienophiles has not been investigated in these reactions. We report here our preliminary results on this subject.

We recently described a three-step synthesis of the angularly trifluoromethylated phenanthrone derivative **1** from trifluoroacetic acid.[2] The key step involved the cycloaddition of 1-trifluoromethyldihydronaphthalene **2**[9,10] with Danishefsky's diene (Scheme 1).[11] The reaction



Reagents and conditions: (i) $Cr(CO)_3(NH_3)_3$ (1.1 equiv., dioxane, 15 h, reflux); (ii) THF 5% of hydroquinone, 15 kbar, 50 °C, 60 h; (iii) sunlight (iv), Me_3SiBr.

Scheme 1

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required high pressure and led to a 1 : 1 mixture of stereoadducts in only 20% yield.

With the aim of improving the yield, the benchrotrenic complex **3** was prepared by refluxing a 0.1 M solution of **2** in dioxane with a 10% excess of $Cr(CO)_3(NH_3)_3$[12] under a flow of argon to remove the ammonia liberated (Scheme 1). Complex **3**, after purification on SiO_2 and recrystallization (pentane–Et_2O), was obtained as orange crystals (77%). The complex **3** was unstable under high pressure (15 kbar) in CH_2Cl_2 but stable in THF solution and was reacted with 2 equiv. of Danishefsky's diene to afford a 70:30 mixture of stereoadducts. Decomplexation readily occurred in natural light in $CHCl_3$ solution and the 10-trifluoromethyl tetrahydrophenanthrone **1** was obtained in 65% yield after hydrolysis and elimination of the methoxy group.

This improved yield demonstrates the activation of styrene derivatives by tricarbonyl chromium and could be of general use. Furthermore the *endo/exo* selectivity is different from that obtained with the uncoordinated dihydronaphthalene **2**, indicating the influence of complexation on the π-stacking between the diene and the aromatic moiety. The preparation of optically active complexes of chromium and their further cycloaddition with dienes or dipoles is under investigation.

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