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OXIDATION OF OLEFINS USING CHROMIC ANHYDRIDE-CHLOROTRIMETHYLSILANE. A CONVENIENT SYNTHESIS OF α-CHLORO KETONES

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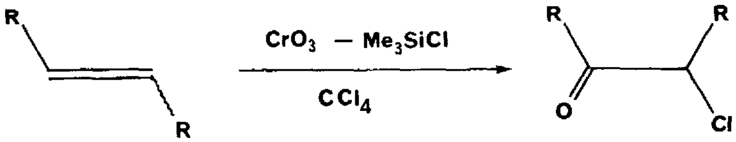
Abstract: Disubstituted internal olefins are oxidized selectively to α-chloro ketones in excellent yields from the reaction with chromic anhydride-chlorotrimethylsilane in carbon tetrachloride.

The chromium oxidation of carbon-carbon double bonds has not been very attractive for preparative purposes, mainly because the reaction tends to produce a mixture of several compounds.[1,2] For example, cyclohexene was found to give cyclohexene oxide, 2-chlorocyclohexanone, 2-chlorocyclohexanol, cyclohexanone, 1,6-hexanedial, and adipic acid in varying yields depending on the structure of the chromium oxidant, reaction media and other reaction conditions.[3] Chromyl chloride seems to be preferable to chromic acid in protic media for the oxidation of olefins, and a couple of excellent procedures were reported by Freeman[4] and Sharpless.[5]

Recently, both chromic anhydride and sodium dichromate were reported to be dissolved in chlorotrimethylsilane-containing dichloromethane.[6] The dissolved chromium species was proved very efficient for the oxidation of alcohols and thiols to the corresponding ketones and disulfides.[6] We reported that this reagent system is also effective for the selective oxidation of arylmethanes to the corresponding aromatic aldehydes.[7]



We report that chromic anhydride-chlorotrimethylsilane combination is superior to any other oxidizing agents for the direct oxidation of a certain type of olefins to the corresponding α-chloro ketones. They have been prepared by either chlorination of the parent ketones,[8] or by direct oxidation of olefins using chromyl chloride.[5]

The procedure is simple and straightforward. The preparation of 2-chlorocycloheptanone is typical. Chromic anhydride (40 mmol) was stirred with chlorotrimethylsilane (40 mmol) in 35 ml of carbon tetrachloride until a dark red homogeneous solution was obtained. Cycloheptene (20 mmol) was added to the mixture cooled to 5-10°C. After stirring 20 hr at room temperature, the whole reaction mixture was chromatograghed through a short column of silica gel with carbon tetrachloride as an eluent. Concentration of the eluted solution under reduced pressure gave 17.8 mmol of 2-chlorocycloheptanone (89%). The reaction conditions and the yields for some α-chloro ketones are listed in Table I.

Chromyl chloride was reported[5] to react very slowly with *cis*-disubstituted olefins in acetone to produce α-chloro ketones in much poorer yield. For example, cyclohexene is known to be oxidized with chromyl chloride in acetone at -78°C to produce 2-chlorocyclohexanone in a mere 38% yield. Using chromic anhydride and chlorotrimethylsilane as an oxidant, both *cis*- and *trans*-disubstituted olefins produced α-chloro ketones equally effectively. Using the present method, cyclohexene can be oxidized to produce 2-chlorocyclohexanone in as much as 83% yield. The oxidation of *trans*-olefins (exclusively) such as 2-octene and cyclododecene was also very successful.

Unsymmetrical disubstituted olefins produced a mixture of both geometrical isomers possible. For example, an equimolar mixture of 2-chloro-3-octanone and 3-chloro-2-octanone was obtained from the oxidation of 2-octene. The reaction was less successful with terminal olefins. α-Chloro aldehydes and ketones were obtained in poor yields.

Some trisubstituted olefins also produced α-chloro ketones, but the yields were only moderate. 2-Methylcyclohexene was oxidized to give 2-chloro-2-methylcyclohexanone in a 68% yield. From the oxidation of 2-phenylcyclohexene, 2-chloro-2-phenylcyclohexanone was obtained in less than 50% yield. A fair amount of 3-phenyl-2-cyclohexenone, an allylic oxidation product, was also formed. This allylic oxidation could not be completely suppressed in the oxidation of these trisubstituted olefins, and the formation of a fair amount of α,β-unsaturated were observed..

For some olefins, oxidative cleavage of carbon-carbon double bonds were observed, especially, at higher reaction temperatures. Stilbene can be oxidized to chlorobenzoin in an excellent yield at room temperature or below. However, refluxing the reaction mixture resulted in the carbon-carbon double bond cleavage, producing benzaldehyde in over 65% yield. Such an oxidative cleavage becomes the major reaction pathway for the oxidation of phenyl substituted terminal olefins. For example, the double bond of styrene and 1,1-diphenylethylene were oxidatively cleaved even at room temperature to produce high yields of benzaldehyde and benzophenone, respectively.

The procedure and reaction conditions can be slightly modified to obtain other useful products. After the oxidation of an olefin was complete, the crude α-chloro ketone might be treated with excess zinc and acetic acid to give the unchlorinated parent ketones[5]. Cyclooctanone was obtained in 79% yield by this method.[10] When the reaction was carried out in methylene chloride containing excess acetyl chloride, acetates of corresponding chlorohydrins were obtained in good yields (60-80%). Not only internal olefins but also terminal olefins such as 1-octene produced the corresponding chlorohydrin acetates.[11] Phenyl-substituted olefins such as styrene were also oxidized satisfactorily without cleavage of double bonds.

Table I. Oxidation of Olefins by CrO_3-TMSCl in CCl_4[a]

Olefin	Time(hr)	Product	%Yield[b]
cyclohexene	18	2-chlorocyclohexanone	83
cyclopentene	18	2-chlorocyclopentanone	84
cycloheptene	20	2-chlorocycloheptanone	89
cyclooctene	20	2-chlorocyclooctanone	87
cyclododecene[c]	22	2-chlorocyclododecanone	85
norbornene	20	2-chloronorbornanone	86
2-octene[c]	17	2-chloro-3-octanone	40
		+ 3-chloro-2-octanone	40
1-octene	17	1-chloro-2-octanone[d]	30
2-methylcyclohexene	18	2-methyl-2-chlorocyclohexanone	68
2-phenylcyclohexanone	15	2-phenyl2-chlorocyclohexanone	50
trans-stilbene	20	chlorobenzoin	70
	20[e]	benzaldehyde	70
styrene	24	benzaldehyde	85
1,1-diphenylethylene	24	benzophenone	91

a. Olefin was reacted with prestirred mixture of 2 equivalents each of CrO_3 and TMSCl. The products were identified by nmr and GC retention time.
b. Yield after column chromatography.
c. Mostly trans isomer.
d. The other oxidation product were not identified.
e. The reaction mixture was refluxed.

Although much work remains to be done to fully understand the nature of this oxidizing system, we strongly believe that the actual oxidizing species is not trimethylsilyl chlorochromate but polyoxochromium dichloride.[12] The reactions of this oxidizing system to many organic functional groups strongly resemble that of chromyl chloride, but the reactivity is much lower. Thus one can carry out the reaction under much milder conditions than those employed for the chromyl chloride oxidation.

Whatever the actual oxidizing species may turn out to be, chlorotrimethylsilane-chromic anhydride combination offers an effective and high yield preparation of α-chloro ketones from both *cis* and *trans*-olefins. The procedure is very convenient. The reaction conditions are mild. The yields are high. Besides, the oxidizing agent can be easily prepared from the readily available inexpensive laboratory chemicals. We are currently investigating other oxidation reactions utilizing this reagent.

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10. Cyclooctene (20 mmol) was reacted with 40 mmol each of chromic anhydride and chlorotrimethylsilane in carbon tetrachloride for 18 hr. The reaction mixture was treated with zinc dust (10 g) and acetic acid (15 ml). After 4 hr stirring at ambient temperature, the reaction mixture was successively washed with water, aq. sodium bicarbonate, and water. Kugelrohr distillation of the concentrated residue gave 14 mmol of cyclooctanone (70%).
11. To a prestirred solution of chromic anhydride (20 mmol), chlorotrimethylsilane(20 mmol), dichloromethane (30 ml), and acetyl chloride (15 ml), was added 1-octene (10 mmol) diluted in dichloromethane (5 ml). After 20 hr stirring at room temperature, excess acetyl chloride and dichloromethane was evaporated under reduced pressure. The residue was rediluted with dichloromethane and filtered through a short column of silica gel. 2-Chloro-1-octyl acetate (7.2 mmol) was obtained upon evaporation of dichloromethane.
12. Polyoxochromium dichloride is believed to be a mixture of $Cl-(CrO_2)_n-Cl$, where n varies depending on the ratio of chromic anhydride and chlorotrimethylsilane. The polymeric chain of chromic anhydride is broken into shorter fragments with the formation of Cr-OTMS and Cl-Cr bonds. The Cr-OTMS bond is unstable and replaced with Cr-Cl in further reaction with chlorotrimethylsilane. The nmr spectrum of the prepared oxidant shows only two types of methyl protons characteristic of chlorotrimethylsilane and hexamethyldisiloxane. In a solution containing an equimolar amount of chromic anhydride and chlorotrimethylsilane, about 35% of Cr-O bond in the polymeric chain is believed to be converted to Cr-Cl.

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