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Chlorotrimethylsilane / Chromium (VI) reagents as new and versatile oxidation systems[1].

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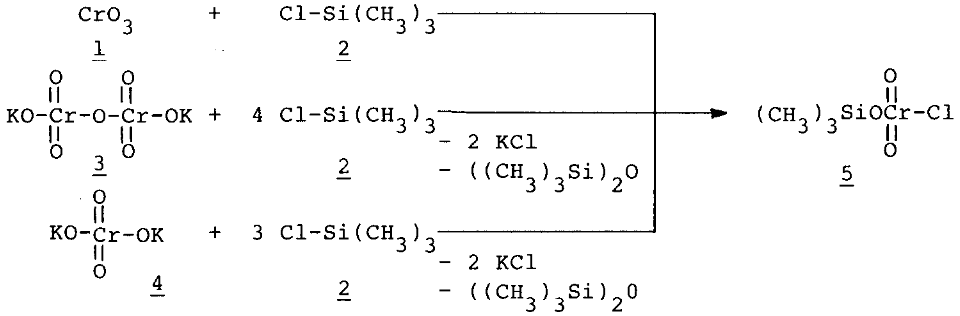
ABSTRACT: Chlorotrimethylsilane-chromium (VI) reagents in acetonitrile or dichloromethane are efficient systems for the oxidation of alcohols to the corresponding carbonyl compounds; they are also highly efficient for the selective oxidation of mercaptans to disulfides and for a mild cleavage of oximes to carbonyl compounds. Trimethylsilyl chlorochromate is suggested as the oxidising active species.

In recent years oxidation with chromium (VI) reagents in anhydrous conditions has found much use in organic chemistry and this importance is reflected in the very wide range of synthetic methods involving the reactions of chromium (VI) derivatives[2-7]. Although some of them are readily available and inexpensive, their use as oxidants in anhydrous conditions is limited by their very low solubility in most organic solvents. We now decribe the preliminary results of an investigation of the oxidation of alcohols, oximes and mercaptans by chlorotrimethylsilane/chromium (VI) reagents under homogeneous phase conditions.

Primary and secondary alcohols are oxidised to aldehydes or ketones in high yields and in a short time by tratment with solutions of potassium dichromate/chlorotrimethylsilane (molar ratio 1:4), potassium dichromate/ chlorotrimethylsilane (1:3) or chromium trioxide/chlorotrimethylsilane (1:1). Formation of the suggested oxidising species formed when chlorotrimetylsilane is added to chromium (VI) reagents is represented in the following scheme:

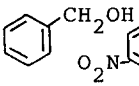
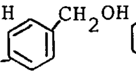
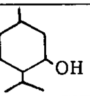
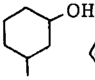
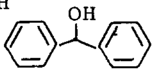
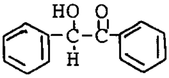
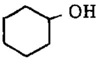


Although no evidence was found for the formation of trimethylsilylchlorochromate as oxidising species, the isolation of hexamethyldisiloxane in nearly quantitative yield from the reaction mixture suggest these reaction pathways[8].

The experimental procedure is exemplified by the oxidation of p-nitrobenzyl alcohol. A mixture of powdered chromium trioxide (1 g, 10 mmol) and trimethylchlorosilane (1.3 ml, 10 mmol) was stirred at room temperature to form an homogeneous orange-red solution which was diluited with dichloromethane (30 ml). p-Nitrobenzyl alcohol (1.53 g, 10 mmol) was then added and the resulting dark brown mixture was stirred at room temperature for 3.5 h. Then, moist silica gel was added and the mixture was filtrated through a pad of silica gel to give a colorless solution which was concentrated under reduced pressure, to afford p-nitrobenzaldehyde (1.31 g, 87%) m.p. 104-106ºC; 106ºC (from dichloromethane/n-hexane)(lit. 104-106)[11]. The use of different alcohols and chromium (VI) reagents permits the preparation of a wide range of carbonyl compounds. The oxidation takes place under anhydrous conditions and the formation of carboxylic acids has not been detected from ^1H n.m.r. and T.L.C. analysis.

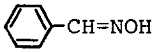
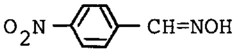
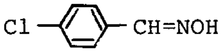
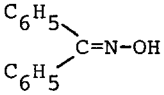
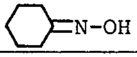
TABLE 1

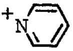
Oxidation of alcohols to carbonyl compounds with $Cl-Si(CH_3)_3/Cr(VI)$ reagents.

Alcohol:							
reagent:	CrO_3	CrO_3	CrO_3	CrO_3	$K_2Cr_2O_7$	$K_2Cr_2O_7$	K_2CrO_4
time (m)[a]	45	210	50	50	20	30	50
yield (%)[b]	81	87	82	95	98	93	88

a. Conditions not optimized b. Isolated yield of pure product. The purity as determined by GLC and ^1H n.m.r. analysis was $\geqslant$ 95%.

TABLE 2

oxime	time[a]	Yield(%)[b,c]
	20m	72
	15h	56[d]
	10m	35[e]
	15m	60
	35m	79
 $(C_6H_5)_2C=N-OH$	1h45m	65
	1.5h	45

a. Conditions not optimized. b. Yield of pure isolated carbonyl compound. c. Carboxylic acids have not been detected by ^{1}H n.m.r. and T.L.C. analysis from the crude reaction mixture. d. ClCrO$_3^-$H$^+$  ; e. ClCrO$_3^-$H$^+$  /H$_2$O$_2$

The wide utility and general superiority of this new oxidation system is exemplified by the fast and mild cleavage of ketoximes and specially aldoximes into carbonyl compounds with no further oxidations. Some examples are given to illustrate this novel procedure for the conversion of oximes to parent carbonyl compounds as is shown in Table 2. We wish to emphasize that the reaction conditions are mild enough to be applied to benzaldoximes which can not be cleaved in good yields by means of similar reagents such as pyridinium chlorochromate[9] or pyridinium chlorochromate/hydrogen peroxide system[10].

We next examined the use of the suggested trimethylsilyl chlorochromate for the selective oxidation of mercaptans. Under similar conditions to those used for oxidations of alcohols or oximes, mercaptans were rapidily oxidised to the corresponding disulfides in excellent yield. As shown (Table 3) this oxidation method may be applied to alkanethiols and arenethiols.

TABLE 3

Compound	T (°C)	time (min)	Yield[a] (%)
Ø-S-S-Ø	-13	15	93
CH_3CH_2-S-S-CH_2CH_3	-13	15	94
$CH_3(CH_2)_2$-S-S-$(CH_2)_2CH_3$	-78	30	96
HOOC-CH_2-S-S-CH_2COOH	-78	30	44

a. Yield of isolated pure product. The purity of all compounds was confirmed by TLC and GLC analysis using a carbowax 20M column.

Nevertheless, under these reaction conditions the reagent is not suitable for performing allylic oxidations, for example benzaldehyde and p-methoxycinnamaldehyde could not be isolated from the respective oxidations of toluene and p-methoxyanetole.

The above results clearly indicate that the chlorotrimetylsilane/ chromium trioxide reagentis a useful alternative to other oxidation reagents. We are continuing to explore the selectivity of this reagent system in a variety of other oxidations and will report the results in due course.

REFERENCES AND NOTES

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8. "Caution": We have attempted the isolation and characterization of the suggested trimethylsilylchlorochromate 5 from chromium trioxide 1 and chlorotrimethylsilane 2, but during distillation a violent explosion took place. The isolation of the product is not convenient and the reactions can be performed in dicloromethane solution without hazard.
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