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REAGENTS AND SYNTHETIC METHODS—40

HALOSILANES/CHROMIUM TRIOXIDE AS EFFICIENT OXIDIZING REAGENTS

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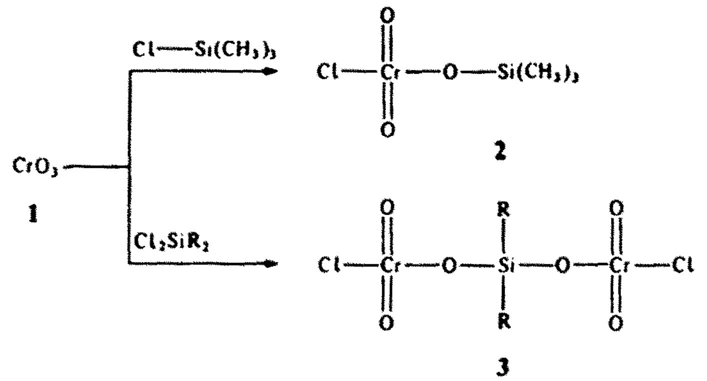
Abstract Synthetic utility of halosilanes-chromium trioxide reagents as excellent new oxidizing agents is described. They are highly efficient for the oxidation of alcohols to carbonyl compounds, for the oxidative coupling of mercaptans into disulfides and for a mild cleavage of oximes to carbonyl compounds. Chlorotrimethylsilane-chromium trioxide has been shown to be an efficient oxidizing agent for the conversion of arylmethanes to benzaldehydes. The reagent is applied to the oxidative cleavage of some benzyl esters. A mild procedure for the iodination of organic compounds by means of *in situ* generated iodonium species from this reagent and molecular iodine is also described.

Oxidation in organic chemistry is apparently of great value as a fundamental process in a wide scope of chemical conversions.[1,2] It remains, however, of considerable interest in the development of new reagents for oxidation reactions and in recent years several papers have described methods which use a chromium (VI) species as oxidizing agent.[3–8] Since the appearance of pyridinium chlorochromate,[3,9] other similar oxidizing agents have been developed varying the amine ligand associated with the chlorochromate anion.

This paper describes the preparation and applications of a new class of chromium (VI) reagents derived from chromium trioxide and halosilanes.



3a $R = CH_3$
3b $R = C_6H_5$

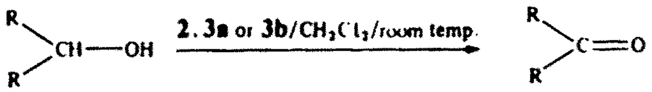
Preparation of the reagents

Treatment of trimethylchlorosilane with powdered chromium trioxide (previously exposed to atmospheric moisture for 5–10 min) in equimolar amounts, gave an orange–red solution which was diluted with dichloromethane. We have attempted the isolation and characterization of the suggested trimethylsilyl chlorochromate **2**, but during distillation a violent explosion took place. Once the reagent formed and diluted with the appropriate solvent (CH_2Cl_2, CCl_4 or 1,2-dichloroethane), dry nitrogen was bubbled through the solution to eliminate traces of hydrogen chloride. The reagent prepared in this way was used for the oxidative transformations required without hazard. The replacement of the trimethylchlorosilane moiety by dimethyldichlorosilane or diphenyldichlorosilane also gives orange–red solutions, but in these cases amounts of chromium trioxide remain in suspension. Although no evidence was found for the generation of the proposed oxidizing species **2** and **3**, we have studied their potential use in a wide variety of oxidation reactions.

Oxidation of alcohols

The trimethylsilyl chlorochromate reagent **2** has been preliminarily reported to be quite suitable for the efficient oxidation of benzylic alcohols and secondary alcohols into the corresponding carbonyl compounds.[10]

Thus, the CO groups were smoothly formed at room temperature by treatment of hydroxy compounds with



the reagent in a molar ratio 1 : 1.5. In this way, the Me groups attached to aromatic rings are not oxidized into the respective formyl groups. The carbonyl compounds were isolated by distillation of the crude reaction mixture, after the evaporation of the hexamethyldisiloxane formed during the work-up.

Similarly, dimethylchlorosilane-chromium trioxide **3a** and diphenyldichlorosilane-chromium trioxide **3b** reagents give the corresponding carbonyl compounds. From the former reagent **3a**, the oxidation reaction is comparable to the trimethylsilyl chlorochromate reagent **2**; however, it proceeded much slower in the case of the latter reagent, and it was conveniently allowed to stir overnight at room temperature to ensure the complete consumption of starting materials. In each case, the conversion was easily monitored by TLC analysis of the crude mixture, and the work-up was simple. Thus, on completion, moist silica gel was added to the mixture; filtration of Cr compounds gave a nearly colorless solution and evaporation of the solvents followed by distillation of the crude mixture afforded the corresponding carbonyl compound. In the case of dimethyldichlorosilane-chromium trioxide reagent **3a**, the mixture was treated with 48% hydrofluoric acid in methanol under reflux conditions before distillation, in order to decompose the siloxane hydrolysis products. For the latter reagent, this treatment was not necessary because the formation of high boiling siloxane compounds, and the reaction products are easily separated by reduced pressure distillation.

The results are compiled in Table 1. As can be seen from the table, diphenyldichlorosilane-chromium trioxide system **3b** is less efficient than the former reagents, probably due to the long reaction time, which permits overoxidations.

We have found the method to be incompatible for the oxidation of primary aliphatic alcohols to the corresponding aldehydes affording complicated mixtures of products, probably on account of their relative facility to undergo secondary oxidations.

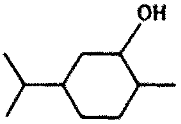
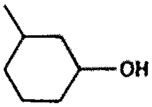
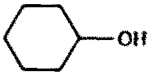
Oxidation of mercaptans

In contrast to most oxidizing agents used in the literature procedures,[11-15] the Cr (VI) reagents have been virtually ignored for the oxidative coupling of thiols to disulfides; there are, however, two brief reports.[5,6] In our methods, thiols reacted smoothly with the reagents to give selectively the corresponding disulfides without overoxidation.

$$\mathrm{R{-}SH} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathbf{2}\ \text{or}\ \mathbf{3a}} \mathrm{R{-}SS{-}R}$$

The reaction is carried out by adding a solution of the oxidizing agent to the corresponding mercaptans in

Table 1. Oxidation of alcohols

Substrate	Reagent	Time	Yield[a,b] (%)
$C_6H_5CH_2OH$	**2**	45 min	81
	3b	60 min	66
$4\text{-}CH_3OC_6H_4CH_2OH$	**3a**	60 min	76
	3b	22 hr	57
$4\text{-}CH_3C_6H_4CH_2OH$	**2**	40 min	93
	3a	1.5 hr	69
	3b	60 min	57
$4\text{-}O_2NC_6H_4CH_2OH$	**2**	3 hr	87
$(C_6H_5)_2CHOH$	**3a**	1.5 hr	92
	3b	4 hr	61
 OH	**2**	50 min	82
 OH	**2**	50 min	95
	3a	1.5 hr	71
	3b	17 hr	58
 OH	**2**	50 min	90
	3b	20 hr	50

[a] Isolated yield of pure products. The purity as determined by GLC and TLC analysis was ≥96%.

[b] M.ps were in agreement with the literature values.[29]

Table 2. Oxidation of mercaptans

Product	Reagent	T (°)	Time (min)	Yield[a] (%)	m.p. (°) or b.p. (°/torr) (lit.)
$\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5$	**2**	−13	15	93	56 58
	3a	−15	60	87	(61-62)[6]
$\text{4-ClC}_6\text{H}_4\text{SSC}_6\text{H}_4\text{Cl-4}$	**2**	−13	15	90	71 72
	3a	−15	60	77	(72 73)[5]
$\text{4-CH}_3\text{C}_6\text{H}_4\text{SSC}_6\text{H}_4\text{CH}_3\text{-4}$	**2**	−10	15	95	42–43
	3a	−15	60	76	(43–44)[5]
$\text{4-CH}_3\text{OC}_6\text{H}_4\text{SSC}_6\text{H}_4\text{OCH}_3\text{-4}$	**2**	−10	15	90	40–42
	3a	−15	60	75	(42–43)[5]
$n\text{-C}_3\text{H}_7\text{SSC}_3\text{H}_7\text{-}n$	**2**	−78	30	96	84–86/23
	3a	−15	60	54	(194/760)[27]
$\text{C}_2\text{H}_5\text{SSC}_2\text{H}_5$	**2**	−13	15	94	152/760 (152/736)[28]
$\text{HOOC(CH}_2)_2\text{SS(CH}_2)_2\text{COOH}$	**2**	78	30	44	152 153 (154)[28]
$\text{C}_6\text{H}_5\text{CH}_2\text{SSCH}_2\text{C}_6\text{H}_5$	**2**	13	30	95	70 72 (70 71)[5]

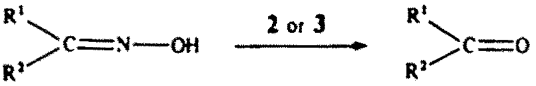
[a] Yield of isolated pure products. The purity (≥97%) of all compounds was confirmed by TLC and GLC analysis using a Carbowax 20M column.

dichloromethane as solvent. If this order is inverted, yields become very poor. As shown in Table 2, this oxidation method may be applied to alkanethiols as well as to arenethiols.

Similarly to the oxidation of 4-methylbenzyl alcohol by means of these reagents, 4-methylbenzenethiol gives 4-methylphenyl disulfide with no further oxidation of the Me group attached to the aromatic ring.

Oxidation of oximes

We next examined the use of these reagents for the oxidative cleavage of some oximes. The generally used procedure for the recovery of the parent ketones or aldehydes from oximes involves treatment of such compounds with pyridinium chlorochromate[16,17] or triethylammonium chlorochromate.[7] The PCC procedure is not very suitable for the regeneration of aldehydes from aldoximes, because overoxidation occurs with this reagent. Pyridinium dichromate also was used for this oxidative cleavage, but carbonyl compounds were not isolated.[18]



The oxidative cleavage of oximes with trimethylsilyl chlorochromate **2** and dimethyldichlorosilane-chromium trioxide **3a** in dichloromethane occurred more quickly than with pyridinium chlorochromate (12–19 hr). The reaction was complete in a brief time in all the cases studied. The results are summarized in Table 3. The generality of the method is indicated by the fact that even benzaldoxime gave a high yield of benzaldehyde without further oxidations; as well as for the other aldoximes tested.

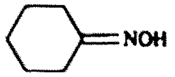
Oxidation of arylmethanes

One of the most important applications of the oxidation of arylmethanes in organic chemistry has been illustrated by the oxidative cleavage of C—N, C—O, C—C and C—H bonds, which has synthetic value in deprotective methods.[19,20]

Although chromyl chloride is the most popular reagent for the oxidation of arylmethanes,[21] there are some disadvantages associated with its use: high cost, difficulty in handling, lack of sensitivity, toxicity and instability. The synthetic utility of **2** as oxidizing agent under homogeneous conditions in non-aqueous solvents, has led us to explore the behaviour of this reagent in the oxidation of some arylmethanes.

As described above, the reagents exhibit an excellent selectivity in the oxidation of 4-methylbenzyl alcohol and 4-methylbenzene thiol without further oxidation.

Table 3. Oxidative cleavage of oximes with halosilanes/chromium trioxide reagents

Oxime	Reagent	Reaction time	Yield[a,b] (%)
$\text{C}_6\text{H}_5\text{—CH=NOH}$	**2**	10 min	72
	3a	2 hr	45
$\text{4-O}_2\text{NC}_6\text{H}_4\text{—CH=NOH}$	**2**	15 min	60
$\text{4-ClC}_6\text{H}_4\text{—CH=NOH}$	**2**	35 min	79
	3a	60 min	66
$(\text{C}_6\text{H}_5)_2\text{C=NOH}$	**2**	105 min	65
	**2**	90 min	45

[a] Yield of pure isolated carbonyl compounds. Carboxylic acids have not been detected by NMR and TLC analyses from the crude reaction mixture.

[b] Yields of redistilled products; siloxane products have not been detected from NMR spectra at high amplitude.

Similarly, we have found that when toluene was shaken with **2** (molar ratio 1 : 3) at room temperature for 24 hr, only 2% conversion into benzaldehyde was observed by GLC analysis of the crude reaction mixture; however, we have found that the oxidation takes place when the reaction is carried out in boiling 1,2-dichloroethane. Under these conditions, we have observed that benzyl chlorides are formed in a competitive reaction process. In order to provide information to consider the likely mechanism of these oxidations, we examined the oxidation of benzyl chloride under similar conditions to those used in the oxidation of toluenes, and we have found that benzaldehyde was obtained in 65% yield. From these results, we assume that the reaction mechanism can involve intermediates such as **4**, **5** and/or **6**, which in the presence of water give the corresponding aldehydes.

The molar ratio of arylmethane to reagent **2**

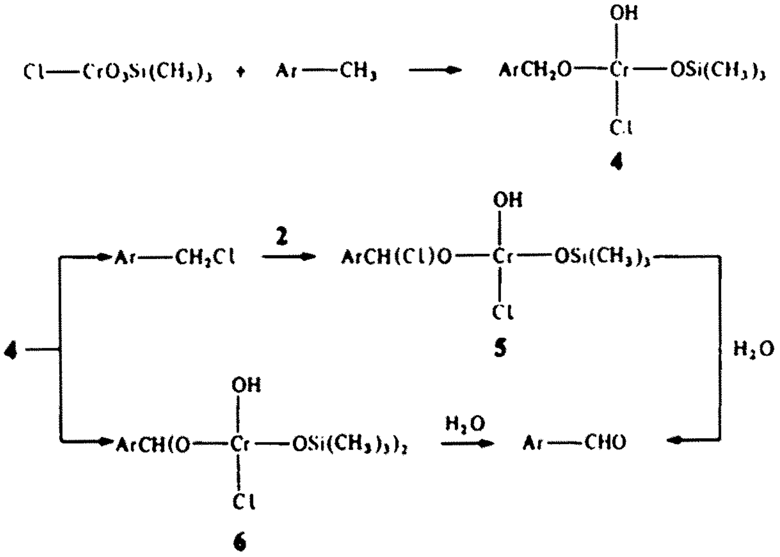
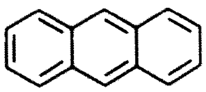
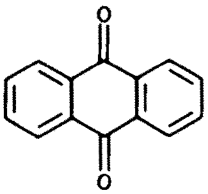
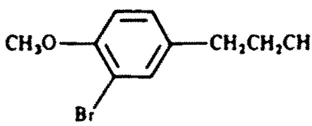
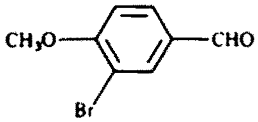
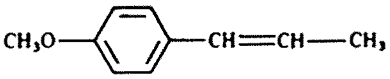
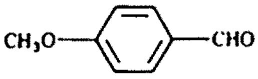


Table 4. Oxidation of arylmethanes with trimethylsilyl chlorochromate reagent **2**

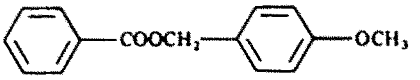
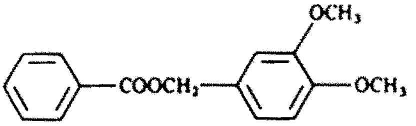
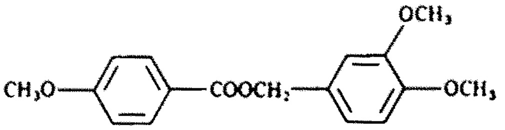
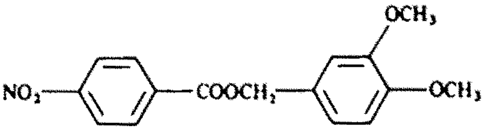
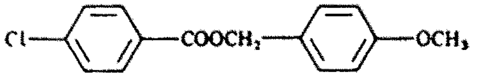
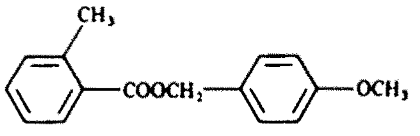
Substrate	Molar ratio (2/substrate)	T (°)	Time	Yield (%)	Product[a]
C_6H_5—CH_3	4 : 1	80	4.5 hr	57[b]	C_6H_5—CHO
4-$ClC_6H_4CH_3$	4 : 1	80	4.5 hr	55[b]	4-ClC_6H_4—CHO
4-$NO_2C_6H_4CH_3$	4 : 1	80	6 hr	[c]	4-$NO_2C_6H_4CHO$
	6 : 1	20	55 min	60	
	10 : 1	15	4.5 hr	83	
	5 : 1	0	1 hr	60	
C_6H_5—CH_2Cl	3 : 1	80	6 hr	65	C_6H_5—CHO

[a] All compounds were identified from their physical and spectroscopic properties, which were in agreement with the literature values.[29]

[b] Isolated as 2,4-dinitrophenylhydrazone derivative; benzyl chloride and 4-chlorobenzyl chloride were characterized as by-products from the crude reaction mixture in a molar ratio (chloride/aldehyde) 1 : 6 and 1 : 7 respectively, determined by NMR analysis.

[c] The starting material was recovered in 97% yield.

Table 5. Benzyl esters cleaved

Substrate	Reagent	Time (hr)	Yield[a] (%)
	2 3a	5 5	70 70
	3a	1	40
	2	5	70
	3a	1	40
	2	5	45
	2 3a	5 5	75 30
	2 3a	5 5	30 35

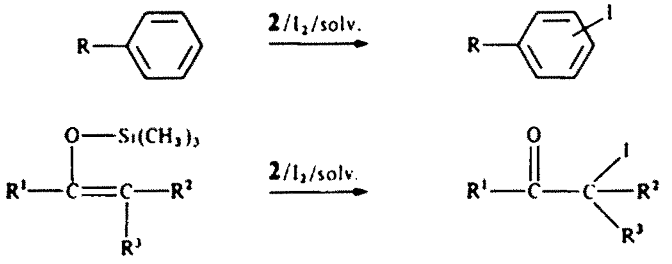
[a] Yield of isolated pure product. The purity checked by NMR and comparison with authentic samples.

necessary for an efficient oxidation was found 1:4, when the molar ratio decreased, the corresponding benzyl chloride was produced in a greater amount.

The results obtained are summarized in Table 4. Under similar reaction conditions, activated arylmethanes (entries 5, 6) undergo facile oxidative dealkylation into the corresponding aldehydes. This fact has special interest for the development of a new deprotective methodology. For example, benzyl esters are oxidatively cleaved into their corresponding carboxylic acids under mild conditions. Thus, treatment of a 4-methoxybenzyl ester or a 3,4-dimethoxybenzyl ester with the reagent **2** or **3** in a molar ratio 1:4 at room temperature, gives after work-up the corresponding carboxylic acids in good yields. Some examples are given in Table 5 to illustrate this procedure for deprotecting benzyl esters. It can be seen from the table that the use of the latter reagent gives lower yields than the former one. On the other hand, it is noteworthy that under similar conditions to those used for this oxidative cleavage, pyridinium chlorochromate was found ineffective for such transformation. Thus, treatment of 4-methoxybenzyl benzoate with pyridinium chlorochromate (molar ratio 1:3) in boiling dichloromethane for 4 hr gave the unchanged starting benzyl ester. These results assume added significance in view of the fact that benzyl esters are often cleaved by reductive methods. One report[22] has been recently described toward oxidative cleavage of benzyl esters by means of triarylamine cation radicals; consequently, our procedure represents the first oxidative cleavage for this class of compounds promoted by chromium (VI) reagents.

Iodination of aromatic compounds and trimethylsilyl enol ethers

The synthetic utility of reagent **2** is further shown by its potential use as a source of iodonium ion by combination of this reagent and molecular iodine in the absence of catalysts. Recent works showed that silver acetate,[23] thallium acetate[24] and copper (II) acetate[25] in combination with molecular iodine are efficient sources of iodonium species. The use of trimethylsilyl chlorochromate **2** resulted in a great enhancement of iodine toward iodination reactions under homogeneous and neutral conditions, probably by the generation of positively polarized iodine.



The results obtained from a variety of substrates are listed in Table 6. According to them, the reaction mechanism can be explained through the iodonium ion formation and subsequent attack of a nucleophile such as chlorochromate anion. This hypothesis is supported by the results recently reported by D'Auria and D'Onofrio[26] on the nucleophilic reactivity of chlorochromate anion toward iodination reactions. In this case, reagent **2** also seems to be more reactive than pyridinium chlorochromate, as shown in the iodination of anisole (entry 2, Table 6). Instead this last reagent gave 4-iodoanisole in 30% yield as the only product in 12 hr, the former reagent produces in a brief time a mixture of iodocompounds which were isolated in comparably higher yields.

CONCLUSIONS

The easy preparation and the synthetic versatility as good oxidizing agents of the reagents reported is obvious as demonstrated here by a rather limited number of examples, and may be readily extended to further applications. Finally, in our opinion, from the results reported, reagent **2** seems to be more suitable than reagents **3a** and **3b**.

EXPERIMENTAL

Preparation of reagents

Trimethylsilyl chlorochromate **2**. Finely powdered CrO_3 (1.0 g, 10 mmol) is exposed to atmospheric moisture for 5–10 min and then chlorotrimethylsilane (1.30 ml, 10 mmol) is added. The mixture is stirred at 30–35° until the formation of a homogeneous orange-red soln (5–10 min) which is diluted with 20 ml of the appropriate solvent (CH_2Cl_2, CCl_4 or $ClCH_2CH_2Cl$). Finally, dry N_2 is bubbled through the soln to eliminate the traces of HCl formed.

Dimethyldichlorosilane-chromium trioxide **3a**. Finely powdered CrO_3 (2.5 g, 25 mmol) is exposed to atmospheric moisture for 5 min and then dimethyldichlorosilane (1.8 ml, 15 mmol) is added. The mixture is stirred at 30–35° until the formation of a heterogeneous orange-red suspension (5–10 min) which is diluted with CH_2Cl_2 (15 ml). Finally, dry N_2 is bubbled through the suspension to eliminate traces of HCl.

Diphenyldichlorosilane-chromium trioxide **3b**. Finely powdered CrO_3 (2 g, 20 mmol) is exposed to atmospheric moisture for 5 min, then diphenyldichlorosilane (2 ml, 10 mmol) is added and the mixture is heated at 45–50° for 5 min. The resulting mixture is diluted with CH_2Cl_2 (10 ml) and dry N_2 is bubbled through the suspension.

Oxidation of alcohols to carbonyl compounds

General procedure for reagent **2**. Over a cooled (0°) soln of **2** (15 mmol) prepared in CH_2Cl_2 as above, the corresponding alcohol (10 mmol) is dropwise added in the same solvent (5 ml) and the resulting mixture is stirred at room temp until the substrate can no longer be detected by TLC (silica gel plates; eluent: n-hexane/AcOEt 3:1). Then, moist silica gel (5 g) is added and the mixture is filtered through a pad of silica gel, dried with Na_2SO_4 and evaporated to afford the crude carbonyl compound, which is purified by recrystallization or distillation.

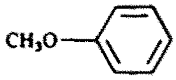
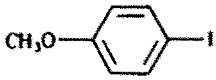
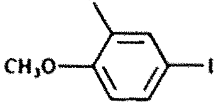
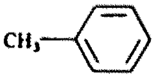
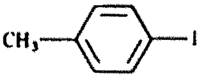
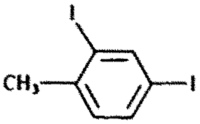
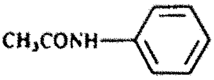
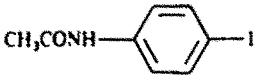
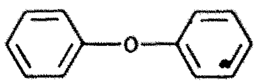
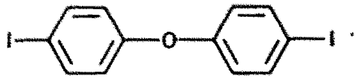
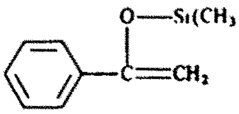
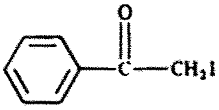
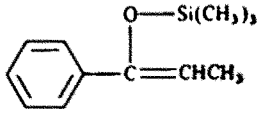
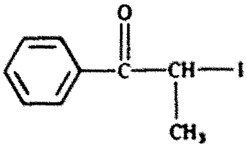
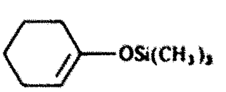
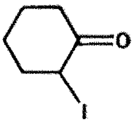
General procedure for reagent **3a**. Over a cooled (0°) suspension of **3a** in CH_2Cl_2, prepared as above, the alcohol (10 mmol) is added in the same solvent (5 ml) and the resulting mixture is stirred at room temp until the alcohol can no longer be detected by TLC. Then, moist silica gel is added (5 g) and the mixture is filtered through a pad of silica gel. Evaporation of the solvent gives a crude mixture of the carbonyl compound and siloxane products. MeOH (10 ml) and 48% HF (1 ml) are added to the mixture and refluxed for 15 min. CH_2Cl_2 (20 ml) and water (20 ml) are added and the organic phase separated, washed with sat $NaHCO_3$ aq and dried with Na_2SO_4. Evaporation of the solvents gives a crude carbonyl compound, which is purified by distillation to afford the pure product.

General procedure for **3b**. The same procedure as that for **2** is followed. In this case, for 10 mmol of substrate **3b** is prepared from CrO_3 (1 g, 10 mmol) and diphenyldichlorosilane (1 ml, 5 mmol) in the same way as described in the preparation of reagents.

Oxidation of mercaptans to disulfides

4-Methylphenyldisulfide. Typical procedure for **2**. A soln of **2** (12 mmol) in CH_2Cl_2 prepared as above is dropwise added

Table 6. Iodinations with trimethylsilyl chlorochromate/iodine system

Substrate[a]	Time[b] (hr)	Yield[c] (%)	Products	m.p. (°) or b.p. (°/torr) (lit.[29])
	5	67		185-190/760 (188/760)
	4		 (51%)	150–155/0.1 (52)
			 (44%)	180 185/0.1
	7	89[e]	 (47%)	150 155/20 (35)
			 (39%)	105 108/20 (211/760)
	3.5	75		179–182 (184)
	3	96		139–141
	1.25	91[f]		unstable[23]
	2	80[f]		unstable
	2	83[f]		57 62/1.5 (58–60/2)[26]

[a] The molar ratio aryl substrate/**2**/I_2 used was 1:2:1.2; the molar ratio trimethylsilyl enol ether/**2**/I_2 used was 1:2:1.5.

[b] Reaction time at room temperature; for entries 1 and 3 reaction was carried out at 40°.

[c] Isolated yields of pure products, the purity as determined by GLC and NMR analyses was $\geqslant 97\%$.

[d] Al compounds were identified by their physical properties (m.p., b.p., IR and NMR spectral characteristics).

[e] Isolated by fractional distillation of the crude reaction mixture.

[f] ^{1}H-NMR ($CDCl_3$) δ ppm: α-iodoacetophenone: 7.38, 7.65 (m, m, 2H, 3H, arom.), 4.20 (s, 2H, CH_2); α-iodopropiophenone: 7.80, 7.32 (m, m, 2H, 3H, arom.); α-iodocyclohexanone: see experimental.

over a cooled soln (−13°) of 4-methylbenzenethiol (2.48 g, 20 mmol) in the same solvent (20 ml), and the mixture is stirred for 20 min. On completion, after general work-up (moist silica gel) the crude 4-methylphenyldisulfide is purified by recrystallization from n-hexane (2.34 g, 95%) m.p.: 42–44° (lit.[5] m.p. 43–44°). ^{1}H-NMR (CCl_4) δ ppm: 2.11 (s, 6H, CH_3), 6.96 (A_2B_2 syst. 8H, arom.).

General procedure for reagent **3a**. A suspension of **3a** prepared as above from CrO_3 (2.0 g, 20 mmol) and dimethyldichlorosilane (1.2 ml, 10 mmol) in CH_2Cl_2 (20 ml) is dropwise added to the mercaptan (15 mmol) in the same solvent (10 ml) at 15°. In general, the reaction is completed within 1 hr (only one product detectable by TLC). After the same work-up as described above for **2**, the crude disulfide is purified as follows:

For solid disulfides: The siloxane hydrolysis products are distilled from the crude mixture under reduced pressure and the solid residue is crystallized from n-hexane to give pure disulfide.

For liquid disulfides: MeOH (10 ml) and 48% HF (1 ml) are added to the crude mixture and refluxed for 15 min. CH_2Cl_2 (20 ml) and water (50 ml) are then added and the organic phase separated, washed with water (20 ml) followed by sat $NaHCO_3$ aq (25 ml × 4) and dried with Na_2SO_4. Evaporation of the solvent, followed by distillation at reduced pressure gives a pure disulfide.

Deoximation of oximes to carbonyl compounds

General procedure for reagent **2**. Over a soln of **2** (20 mmol) prepared in CH_2Cl_2 as above, the corresponding oxime (10 mmol) is added in the same solvent (5 ml) and the mixture is stirred at room temp until the substrate can no longer be detected by TLC (silica gel plates; eluent: n-hexane-AcOEt 2:1). On completion, after the general work-up (moist silica gel) the crude carbonyl compound is purified by recrystallization or distillation.

General procedure for reagent **3a**. Over a mixture of **3a** prepared as described from CrO_3 (25 mmol) and dimethyldichlorosilane (15 mmol), the corresponding oxime (10 mmol) is added in the same solvent (5 ml). The resulting mixture is stirred at room temp until the substrate can no longer be detected by TLC. The same work-up followed for the oxidation of alcohols to carbonyl compounds is suitable.

Oxidation of arylmethanes to benzaldehydes

General procedure for reagent **2**. Over a soln of **2** (20 mmol) prepared in 1,2-dichloroethane as above, the corresponding arylmethane (5 mmol) is added and the mixture is stirred at reflux until the substrate can no longer be detected by TLC. On completion, after the general work-up (moist silica gel) the crude aldehyde is purified by recrystallization or distillation.

Anthraquinone. A mixture of powdered CrO_3 (3.0 g, 30 mmol) (previously exposed to atmospheric moisture for 5 min) and trimethylchlorosilane (3.84 ml, 30 mmol) was stirred at room temp to form a homogeneous orange red soln which was diluted with 1,2-dichloroethane (20 ml). Dry N_2 was bubbled through the soln and then anthracene (0.89 g, 5 mmol) was added and the resulting dark brown mixture was stirred at room temp for 55 min. Then, moist silica gel (5.0 g) was added and the mixture filtered through a pad of silica gel to give a yellow soln which was concentrated under reduced pressure to afford anthraquinone (0.62 g, 60%), m.p.: 283–284° (lit.[29] m.p. 286°).

Oxidative cleavage of benzyl esters

General procedure for reagent **2**. Over a soln of **2** (20 mmol) prepared in CH_2Cl_2 as above, the corresponding 4-methoxybenzyl ester (5 mmol) is added, and the mixture is stirred at room temp for 5 hr. On completion, the mixture is taken up over a 1 N $NaHSO_3$ soln (60 ml), the organic layer being separated, and the aqueous phase extracted with EtOAc (10 ml × 2). The combined organic solns are extracted with 1 N NaOH (10 ml × 2) and the basic soln is acidified (HCl) to obtain the crude carboxylic acid, which is purified by crystallization.

General procedure for reagent **3a**. The same procedure as that for reagent **2** was used. In this case, for 5 mmol of substrate, the reagent **3a** was prepared from chromium trioxide (2 g, 20 mmol), dimethyldichlorosilane (1.2 ml, 10 mmol) and dichloromethane (20 ml) in the same way as described above.

Iodination of aromatic compounds

General procedure for reagent **2**. Over a soln of **2** (20 mmol) prepared in CH_2Cl_2 as above, I_2 (3.05 g, 12 mmol) and a soln of the corresponding aromatic compound (10 mmol) in the same solvent (5 ml) are added and the mixture is stirred at room temp until the substrate can no longer be detected by TLC. Upon completion of the reaction, moist silica gel is added to hydrolyze the oxidant, and the mixture is filtered through a pad of silica gel and washed with 2 N $NaHSO_3$ (25 ml × 2) before being dried (Na_2SO_4) and evaporated to afford the crude iodo derivative, which is purified by distillation or crystallization.

Synthesis of α-iodoketones

General procedure for reagent **2**. The same procedure as in the iodination of aromatic compounds is followed, but using the corresponding trimethylsilyl enol ether (10 mmol) as substrate, and 15 mmol of I_2 instead of 12 mmol.

α-Iodocyclohexanone: typical procedure. Over a soln of **2** (10 mmol) prepared in CH_2Cl_2 (15 ml), iodine (1.9 g, 15 mmol) and a soln of 1-trimethylsiloxycyclohexene (0.85 g, 5.0 mmol) in the same solvent (5 ml) are added at 0°. After stirring for 2 hr, moist silica gel (5.0 g) is added and the mixture is filtered through a pad of silica gel and washed with 2 N $NaHSO_3$ (20 ml) before being dried (Na_2SO_4). Evaporation of the solvent affords crude α-iodocyclohexanone, which is purified by reduced pressure distillation (1.12 g, 83%) (b.p. 57–62°/1.5 Torr) (lit.[26] b.p. 58–60°/2 Torr). NMR ($CDCl_3$) δ ppm: 4.48 (t, 1H, CH), 2.84 (m, 2H, CH_2CO), 1.85, 2.15 (m, m, 6H, CH_2).

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