

THE GENERATION OF CARBONYL COMPOUNDS FROM ACETALS AND KETALS BY IODOTRICHLOROSILANE (ITCS)

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Abstract. Cheap and readily available iodotrichlorosilane ($\text{SiCl}_4 / \text{NaI}$) readily regenerates aldehydes and ketones from cyclic and acyclic acetals and ketals, in 20-60 min at ambient temperature. The reaction is highly chemoselective as phenolic ethers and esters are not cleaved. The pathway for the process is unlike any previously proposed.

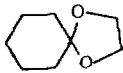
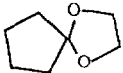
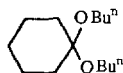
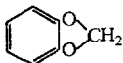
The generation of carbonyl compounds from *gem*-diethers is an important process that is of continuing interest. Transacetalisation¹⁻⁴ and hydrolysis with a wide variety of acid catalysts⁵⁻¹⁰ are the traditional methods of choice. Anhydrous methods include the use of derivatives of titanium,¹¹ aluminium,¹² zirconium,¹³ samarium,¹⁴ tin,¹⁵ phosphorus¹⁶ and boron¹⁷ as well as oxidation with triphenylcarbonium tetrafluoroborate.¹⁸ Iodotrimethylsilane can be used for the high yield cleavage of *acyclic* ketals, but is unsuitable for cyclic ketals¹⁹ whilst diiodosilane may, in some cases, be used at low temperatures but above 0°C it produces iodoalkanes.²⁰

We have recently reported two unique reactions involving iodotrichlorosilane (ITCS)^{21,22}, a reagent readily available by mixing cheap, commercially available tetrachlorosilane with sodium iodide. For experimental purposes the mixture may be used in place of isolated ITCS.

We now report that ITCS (but not tetrachlorosilane) readily cleaves both cyclic and acyclic acetals and ketals at room temperature in 20-60 min.²³ Our results are given in the Table.

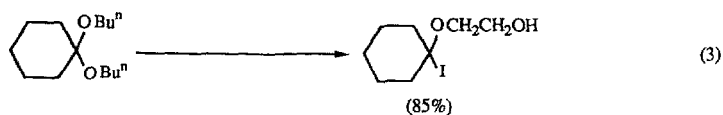
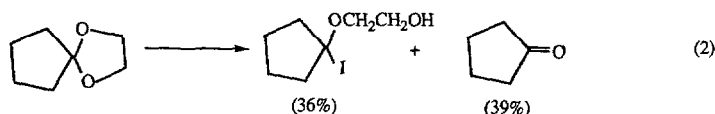
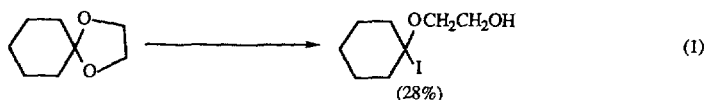
The reactions with acetals are very fast as, even though ITCS readily cleaves esters²³ and phenolic methyl ethers²⁴, both of these groups survive the deacetalisation process (Table, exp. 4, 5). Unlike iodotrimethylsilane, ITCS is suitable for the cleavage of dioxolanes derived from either aldehydes or ketones (Table, exp. 3, 6, 7) as well as for the cleavage of acyclic *gem*-diethers (Table, exp. 1, 2, 4, 5, 8).

TABLE
Cleavage of 1,1-diethers by ITCS

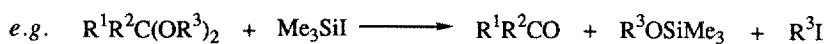
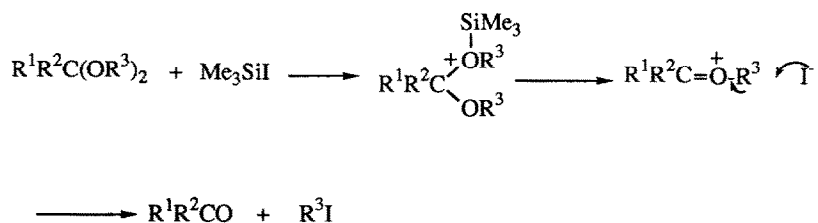
Experiment ^{a,b}	Substrate	Time (min)	Product	Yield(%) ^c
1	PhCH(OEt) ₂	20	PhCHO	95
2	PhCH(OBu ⁿ) ₂	20	PhCHO	91
3	2-Phenyl-1,3-dioxolane	20	PhCHO	81
4	3-MeO ₂ C.C ₆ H ₄ CH(OMe) ₂	20	3-MeO ₂ C.C ₆ H ₄ CHO	74
5	2,5-di-MeOC ₆ H ₃ CH(OMe) ₂	20	2,5-di-MeOC ₆ H ₃ CHO	70
6		30	Cyclohexanone	76
7		30	Cyclopentanone	86
8		30	Cyclohexanone	73
9		60	1,2-Dihydroxybenzene	86

^aAll reactions carried out at r.t. (ca. 23°C). No attempts at optimisation made. ^bTwo equivalents of ITCS to *gem*-diether were used. ^cAll yields are of isolated, purified, fully characterised products.

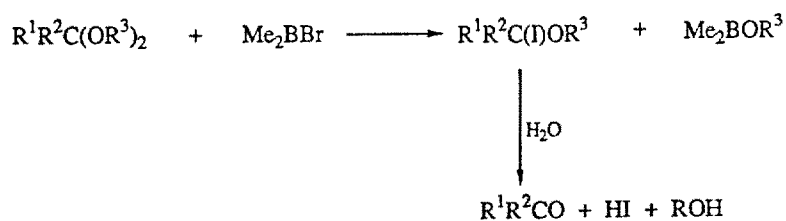
The following observations are relevant in delineating the pathway for the process. (1) Two equivalents of ITCS are required for efficient production of the carbonyl compounds. (2) An equivalent of iodine is produced in the reaction. (3) In experiment 8 (Table), no butyl iodide is produced. (4) The carbonyl products are present *prior* to water addition. (5) When one equivalent of ITCS is used, then α -iodoethers can be isolated (eq. 1, 2 and 3). (6) The isolated α -iodoethers react extremely rapidly with an equivalent of ITCS to yield the corresponding carbonyl compounds and iodine. Once more²¹ ITCS is acting as a redox reagent.



These observations completely rule out a pathway analogous to either Scheme 1¹⁹ or Scheme 2.¹⁷

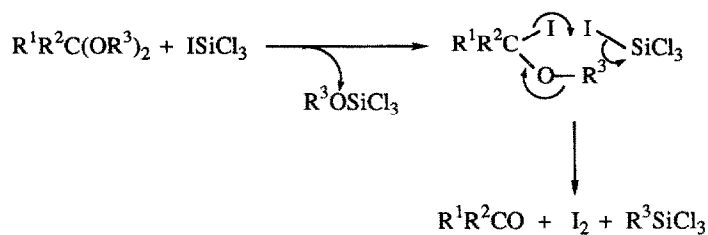


Scheme 1



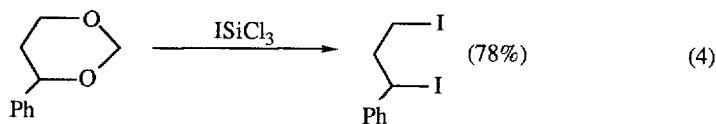
Scheme 2

Instead, we propose Scheme 3 as a working hypothesis that fits all the known data for the general experiments 1-8.



Scheme 3

We have two examples (Table 1, exp. 9) and equation 4 of formaldehyde derived acetals interacting with ITCS by different pathways. These interesting deviations are receiving attention.



In summary, carbonyl regeneration from acetals and ketals using ITCS is a mild, general, chemoselective procedure that uses a cheap, readily available reagent. As such, the process should find wide application.

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