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Use of reductive properties of iodotrichlorosilane II: Chemoselective reduction of α,β-unsaturated ketones and nitriles

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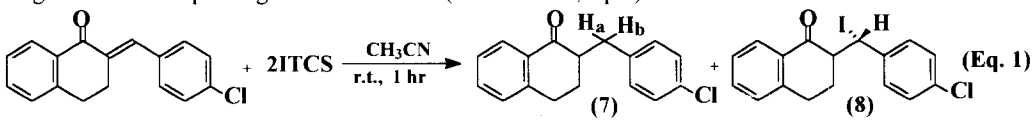
Abstract: *A new synthetic procedure for the selective reduction of α,β-unsaturated ketones and nitriles, using iodotrichlorosilane (ITCS generated in situ from $SiCl_4$-NaI) under mild conditions to produce the corresponding saturated ketone and nitrile compounds in quantitative yields, is described.*

A tetrachlorosilane-sodium iodide has been applied to a variety of organic synthesis as an iodotrichlorosilane (ITCS) equivalent[1], where beside the application to cleavage of ethers, esters[1], acetals and ketals[2], it can be used to introduce an acetamide or benzamide group into aromatic or aliphatic aldehydes to produce corresponding derivative containing a nitrogen function in the place of the oxygen function of its carbonyl group[3-5]. Recently we reported[6] the selective reduction of phenolic quinones to their parent phenolic ketones by using iodotrichlorosilane ($SiCl_4$-NaI in situ).

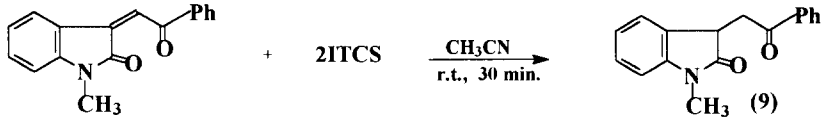
In an endeavor to extend the scope of the ITCS reagent in organic synthesis, we have found that β-phenyl α,β-unsaturated ketones can be reduced to the corresponding saturated ketones (compounds 1-3 & 5-6) in high yields by using two equivalents of ITCS.

Unlike diiodosilane[7], 1,4-addition to produce the β-iodo ketones were the only observed reaction of α,β-unsaturated ketones with ITCS and no by-products (1,3-diiodo derivatives) were detected. β-Iodo ketones (e.g compounds 4 & 8) are stable for long periods under the reaction conditions and can be isolated along with the corresponding saturated ketones (entries 3 & 6, eq. 1).



(Eq. 1)

Following up that reaction, the reaction succeeded with 1-methyl-2-oxoindolin-3-ylideneacetophenone to give 1-methyl-3-phenacyl-2-oxoindole (9) in quantitative yield (eq. 2). So the reaction conditions, allow sensitive functional groups like lactame ring to be carried through.



(Eq. 2)

Table 1 demonstrates the generality of using ITCS reagent in the reduction of various aliphatic and aromatic α,β-unsaturated ketones to give corresponding saturated ketones in quantitative yields and under mild conditions (entries 1-9). Instead of chlorotrimethylsilane-sodium iodide reagent[8] or chlorotrimethylsilane sodium iodide-water reagent[9], ITCS is applicable to reduce enones possessing two alkyl substituents at the α-position of the double bond (entry 10).

It is also studied the reaction with benzalmalononitrile derivatives (entries 11,12). They were selectively reduced at the double bond to give benzylmalononitrile derivatives (compounds 10 & 11) under

reflux in good yields (Table 1).

Table (1) Reduction of α,β-unsaturated ketones and nitriles by ITCS (TCS-NaI in situ) in acetonitrile.

Entry no.	Substrate	time (min)	Product[a]	Yield (%)
1.	Benzalacetophenone	40	1,3-Diphenylpropan-1-one **(1)**	95
2.	4'-Methoxybenzalacetophenone	30	3-(4-Methoxyphenyl)-1-phenylpropan-1-one **(2)**	95
3.	4'-Chlorobenzalacetophenone	30	3-(4-Chlorophenyl)-1-phenylpropan-1-one**(3)** + 3-iodo-3-(4-chlorophenyl)-1-phenyl-propan-1-one **(4)**	60 30
4.	4'-Methoxybenzalacetophenone	20	1-(4-Methoxyphenyl)-3-phenylpropan-1-one **(5)**	94
5.	2-Benzal-1-tetralone	20	2-Benzyl-1-tetralone **(6)**	90
6.	2-(4-Chlorobenzal)-1-tetralone	60	2-(4-Chlorobenzyl)-1-tetralone **(7)** + 2-[Phenyl(iodomethyl)]-1-tetralone **(8)**	70 20
7.	2-(4-Methoxybenzal)-1-tetralone	30	2-(4-Methoxybenzyl)-1-tetralone	93
8.	2-(4-Hydroxybenzal)-1-tetralone	30	2-(4-Hydroxybenzyl)-1-tetralone	90
9.	1-Methyl-2-oxoindolin-3-ylideneacetophenone	30	1-Methyl-3-phenacyl-2-oxoindole **(9)**	94
10.	Mesityl oxide	35	4-Methyl-2-pentanone	90
11.	4-Chlorobenzalmalononitrile	60	4-Chlorobenzylmalononitrile[10] **(10)**	81
12.	3-Chlorobenzalmalononitrile	95	3-Chlorobenzylmalononitrile **(11)**	72

a)The reactions of entries 1 to 10 were carried out as in the typical experimental procedure at room temperature while the reactions of entries 11 and 12 under reflux.

In a typical procedure, tetrachlorosilane (20 mmol) was added to a mixture of 1-Methyl-2-oxoindolin-3-ylideneacetophenone (10 mmol) and sodium iodide (20 mmol) in acetonitrile (15 ml), the mixture was stirred at ambient temperature. It was poured into water (50 ml) and extracted with chloroform (2 x 50 ml) the extracts were washed with sodium thiosulphate solution (15 ml, 10%) to remove the color of iodine, dried over anhydrous K_2CO_3, and the solvent was removed by distillation, the residue was purified by column chromatography to give 1-Methyl-3-phenacyl-2-oxoindole (9) [m.p. = 135°C].

The method offers the significant advantages that the reagent is inexpensive and the reaction can be done conveniently with two moles of ITCS. It appears to be general and applicable to derivatives of α,β-unsaturated ketones and nitriles. The reduction of enones with ITCS has great value in that the yields are high using extremely mild conditions, which allow sensitive functional groups to be carried through.

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10. The ^1H NMR of compound 10 showed a triplet at δ3.94 for CH and a doublet at δ 3.21 for CH_2. ^{13}C-NMR showed the CH group at 35.65, and $-CH_2-$ group at 24.82. Further evidence was obtained from its mass spectrum which showed the parent peak at m/z 190 (M^+).

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