Direct Oxidation of Benzylic and Allylic Silyl Ethers to Carbonyl Compounds

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Abstract: Oxidation of benzylic or allylic silyl ethers with DDQ under UV irradiation leads directly to the corresponding carbonyl compounds with moderate to good yields.

The synthesis of silyl ethers represents one of the most popular procedure to protect the hydroxy function¹. Usually their conversion to the corresponding carbonyl derivatives requires a previous deprotection step. However many examples of direct oxidation have been reported. Among them, the Collins oxidation of primary trimethylsilyl ethers led selectively to aldehydes², whereas oxidation of secondary trimethylsilyl ethers according to Jones procedure or with pyridinium chlorochromate give ketones with high efficiency³. Selective oxidation of primary trisethylsilyl ethers has been achieved using Swern conditions in prostanoid synthesis⁴. Other methods recently published required unusual or expensive reagents⁵⁻⁷ not always compatible with other functionalities. Finally, in the case of benzylic silyl ethers, oxidation was also observed with NBS⁸ and recently reinvestigated under thermal conditions⁹. Unfortunately, α -bromoketones were also isolated as by-products.

We report here a new process to convert selectively allylic or benzylic silyl ethers 1 or 3 to the corresponding ketones 2 or aldehydes 4 under U.V. irradiation and in presence of 2,3-dichloro-5,6-dicyanoquinone (DDQ).



To our knowledge, only one example of oxidation of silyl ethers using DDQ has been reported. It is conducted under thermal conditions with acetic acid as solvent and under these conditions previous deprotection of the trimethylsilyl group is assumed¹⁰.

In order to oxidize selectively allylic or benzylic silyl ethers without modification of other functionalities strong acidic conditions had to be avoided. Acetonitrile which was choosen as solvent at the beginning of this work has been replaced avantageously by a mixture methylene chloride and acetonitrile (9/1). After a short time of irradiation in this solvent there is total conversion of the substrate and precipitation of the reduced form of DDQ which can be easily removed by simple filtration. The results are summarized in the table 1.





(a) yield of pure isolated material based on 1

To test the photochemical assistance in this reaction, 1-phenyl 1-trimethylsilyloxy propane 1a was submitted to the oxidation conditions in presence of light and in the dark. The results are collected in Table 2.

After 3h40, for run 1, starting material was totally consumed and converted to 2a with 85% yield, in the dark (run 3) very low conversion was observed. Other potential hydrogen abstractors such as DCB and DBTP were far less efficient than DDQ (run 5 and 6).

Table 2



1a



2a

run	oxidizing agent	solvent	conditions	time	2a/1a ^(a)
1	DDQ	CH ₂ Cl ₂ / CH ₃ CN	hυ	0h45	77 / 23
				1h45	86/14
				3h40	>99/1
2	DDQ	CH ₃ CN	hu	3h40	57 / 43
3	DDQ	CH_2Cl_2/CH_3CN	dark	3h40	8 / 92
4	DDQ	CH ₂ Cl ₂ / CH ₃ CN	hu	0h45	48 / 52
				1h 45	78/22
	+ K_2CO_3 (1eq)			3h40	90 / 10
5	DCB ^(b)	CH ₃ CN	hu	3h40	8/92
6	DBTP ^(¢)	CH ₃ CN	hu	3h40	0/100

(a) determined by GC analysis on the crude product (c) DBTP⁻ di-t-butylterephtalate (b) DCB 1,4 dicyanobenzene.

When the reaction is performed in the presence of one equivalent of potassium carbonate, the rate of the reaction is considerably slower. This observation could reflect that catalytic amounts of hydrochloric acid could be formed by a competive photolysis of methylene chloride; the silyl ethers might then be cleaved prior to the oxidation step. Indeed, in the case of substrate 1h and before total conversion, a G C. analysis of the crude mixture shows clearly the formation of small amounts of the corresponding alcohol. Furthermore alignatic trimethylsilyl ethers of menthyl or 3-phenylpropyl undergo only deprotection when irradiated under the typical conditions. Mechanistically, two different pathways might simultaneously occur: the direct oxidation of the silyl ether as recently shown in the case of benzylarylethers^{11,12} and a complementary process *via* preliminary deprotection step followed by oxidation of the alcohol.

Unlike the NBS oxidation⁹, the formation of by-products in the case of secondary silyl ethers was not observed. The presence of other labile functions was compatible with the reaction conditions. For example no photochemical cleavage of the C-Br bond was observed when 2-bromo 1-(trimethylsilyloxy)-indane 1g was submitted to irradiation Moreover, the oxidation of benzylic trimethyl silyl ethers is selectively observed without deprotection of bulkier silyl ethers ¹³.

In conclusion, assistance of light is highly beneficial to the oxidation of allylic or benzylic trimethylsilyl ethers with DDQ.

Typical procedure:

To a solution of sulplether (3.5 mmol) in methylene chloride (90 ml) is added a solution of DDQ (3.5 mmol) in acetonitrile (10 ml). This mixture is poured into quartz tubes, degassed with argon and irradiated at 254 nm in a Merry-go-round type of system (Rayonnet) for 3 hours (TLC control). After filtration, the solvent is removed by distillation and the crude product purified by flash-chromatography (SiO₂, eluent AcOEt / Petrol ether 5/95)

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- A similar selectivity was already observed in case of the chromic oxidation of silyl ethers (Ref. 3a). 13

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