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SELECTIVE DEPROTECTION OF DIPHENYLMETHYLSILYLETHERS OF ALLYLIC AND BENZYLIC ALCOHOLS

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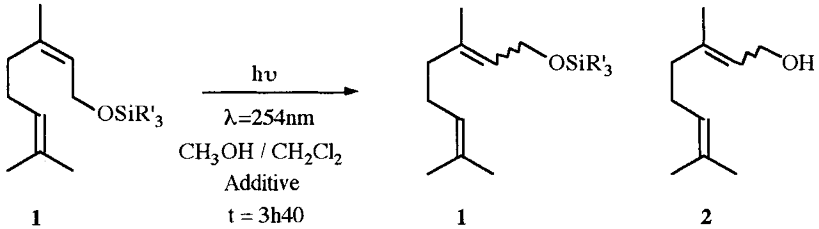
Abstract: Selective deprotection of diphenylmethylsilylethers of allylic or benzylic alcohols is achieved by U.V. irradiation in presence of phenanthrene (1eq.) in methylene chloride and methanol. Under these conditions, other ethers containing the t-butyldimethylsilyl or the t-butyldiphenylsilyl group are recovered unmodified.

Silyl ethers constitute one of the most convenient methods to protect an hydroxy function [1,2]. Among all the silyl groups available, t-butyldimethylsilyl (TBDMS)[3], diphenylmethylsilyl (DPMS)[4] and t-butyldiphenylsilyl (TBDPS)[5] are the most used in synthesis. However, up to date, few methods to selectively remove one of these groups in the presence of the others have been reported [6]. Otherwise, in connection with [2+2] photocycloaddition studies between allylic silylethers and enones, we have observed under irradiation and in some cases, efficient cleavage of the ether function to the corresponding alcohol. Because of the great importance of selective deprotection of ethers in organic synthesis, we decided to study the photobehavior of various allylic silylethers under UV irradiation in the presence of additives. We report here the efficient and selective photodeprotection of allylic or benzylic DPMS

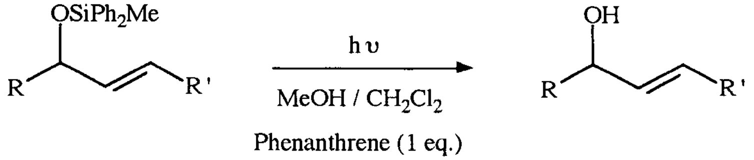
Table 1: Photobehavior of silyl ethers of nerol.



1 **1** **2**

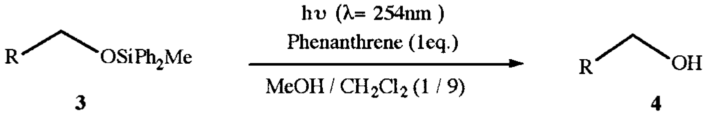
Substrate	Additive	G.C. Ratio 1	2
1a	no	0	100
R_3Si=TBDMS	phenanthrene (1eq.)	88	12
1b	no	0	100
R'$_3$Si = DPMS	phenanthrene (1eq.)	0	100
1c	no	100	0
R'$_3$Si = TBDPS	phenanthrene (1eq.)	100	0

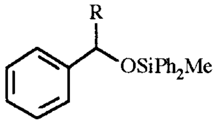
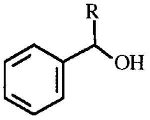
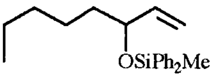
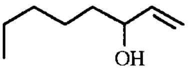
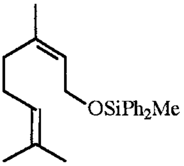
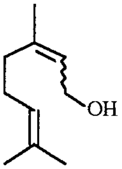
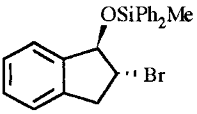
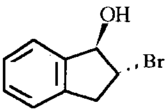
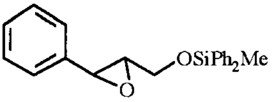
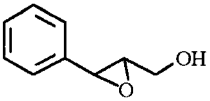
ethers performed in a solution of methylene chloride and methanol, with one equivalent of phenanthrene.



Initially, we have studied the silylethers **1a** (R_3Si = t-BuMe$_2$Si), **1b** (R_3Si = Ph$_2$MeSi) and **1c** (R_3Si = t-BuPh$_2$Si), easily prepared from nerol according to the standard procedures [3-5]. Irradiation at 254 nm in a mixture of methylene chloride and methanol (9:1) of these compounds leads after only one hour to the corresponding alcohol, totally for ethers **1a** and **1b** and not at all for **1c** (Table 1). These results are consistent with the reactivity of silylethers in protic medium[7,8]. Performed in the presence of one equivalent of phenanthrene, results are more surprizing; after the same time of irradiation, **1a** and **1c** are essentially or totaly

Table 2: Deprotection of allylic and benzylic diphenylmethylsilyl ethers:

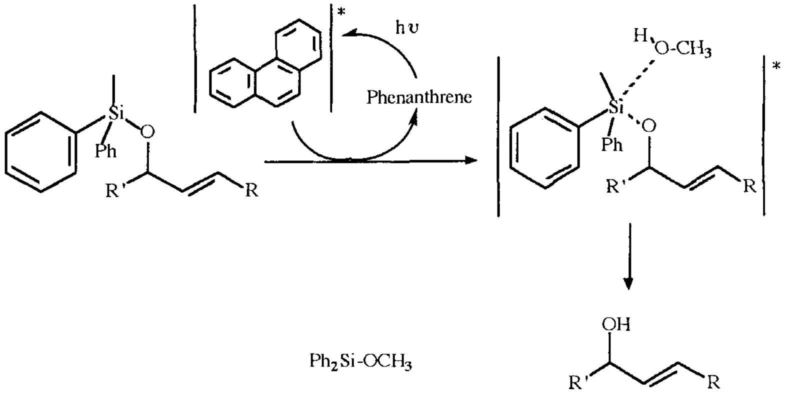


Substrate	**Conditions**[a]	**Product**	**c.y.(%)**[b]
			
3a (R = Me)	hν	**4a**	**84**
3b (R = Et)	hν	**4b**	**73**
3b (R = Et)	hν+ Et$_3$N (1eq.)	-	**0**
			
3c	hν dark	**4c** no reaction	**83** -
			
3d	hν	**4d**	**89**
			
3e	hν	**4e**	**78**
			
3f	hν	**4f**	**51**

(a) standard procedure reaction. (b) isolated yields recovered as a mixture of geometric isomers, while an efficient deprotection is observed for **1b**.

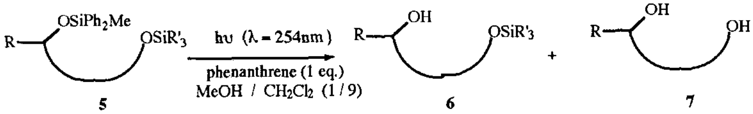
This reaction has been generalized to other allylic or benzylic silylethers and all cases efficient deprotection of the DPMS ether is observed, usually after only one to three hours of irradiation (Table 2).

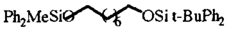
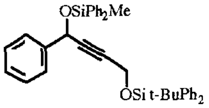
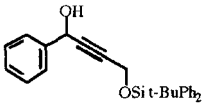
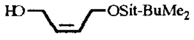
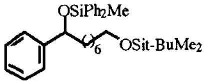
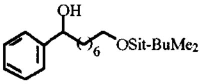
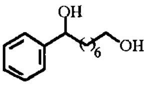
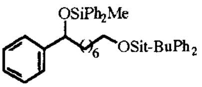
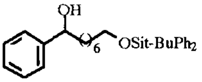
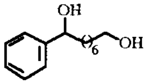
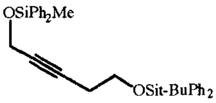
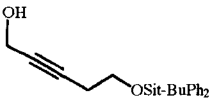
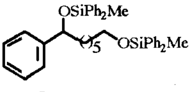
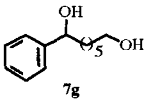
Assistance of light is necessary to perform the reaction; for example, ether **3c** is efficiently deprotected by irradiation under the mentioned conditions, whereas in the dark, the same substrate is entirely recovered. The reaction is only efficient with allylic or benzylic diphenylmethylsilylether. For example,with α,β-epoxy ether **3f**, deprotection takes place, but the corresponding alcohol is isolated in only 51% yield after 7 hours of irradiation. For all non-allylic or non-benzylic ethers, either no deprotection occurs or a sluggish reaction is observed over a long time of irradiation. Surprisingly, the presence of a bromide atom is compatible with the irradiation conditions[9] and ether **3e** is conveniently deprotected without cleavage of the C-Br bond. Mechanistically, methanol is necessary to promote the reaction and as by-product, we observed the formation of DPMS-OMe, thus methanol might play the role of nucleophile[10] as illustrated in the following scheme.



However, the acidic cleavage of silyl ether can also be considered. Photolysis of methylene chloride is known to give traces of hydrogen chloride[11], which is able to

Table 3: Selective deprotection of bis(silyl)ethers



Substrate	Conditions$^{(a)}$	Product	C.y.$^{(b)}$
 **5a**	hν/A	no reaction	-
 **5b**	hν/A	 **6b**	64
 **5c**	hν/A	 **6c**	68$^{(c)}$
		 	
5d	hν/A	**6d** **7d**	85 11
5d	hν/B	**6d** **7d**	- 72
		 	
5e	hν/A	**6e** **7e**	86 -
	nBu$_4$NF / THF	**6e** **7e**	- 95
 **5f**	hν/A	 **6f**	64
 **5g**	hν/A	 **7g**	73

[a] hν / A : irradiation performed with phenanthrene.
hν / B : irradiation performed without phenanthrene.

[b] Yields of isolated pure compounds.

[c] No formation of diol detected.

cleave the TBDMS and DPMS silyl ethers[8]. This hypothesis is supported by the unreactivity of ether **3b** when irradiated in the presence of a base such as triethylamine. In this case, the base could react with the HCl, leading to ammonium salts, which are then too weakly acidic to promote the cleavage of the O-Si bond. Otherwise under our conditions, it is now possible to deprotect selectively one allylic ether without concomitant cleavage of other silyl ethers such as TBDMS or DPTBS (Table 3). The photobehavior of ether **5d** in the presence of phenanthrene (conditions hυ/A) or in its absence (cconditions hυ/B) shows clearly the importance of the additive. Without phenanthrene, only the diol is isolated after irradiation. Furthermore, during nucleophilic attack by fluoride, the standard method to deprotect the silyl ethers[1], no selectivity appears during the deprotection of the compound **5e**. Unselective deprotection of the bis(DPMS) ether **5g** could be explained by a first deprotection of the allylic ether followed by an intramolecular migration of the terminal silyl group to the activated position and finally cleavage of the labile ether function to the diol **7g**. Unfortunately, no evidence of this possibility has been yet observed when the reaction is followed by GC analysis.

In conclusion, we have developed an efficient and selective cleavage method of DPMS ethers of allylic or benzylic alcohols. We expect that this method will be useful in synthesis.

Experimental procedure:

The diphenylmethylsilylether (3.5 mmol) and phenanthrene (3.5mmol) are dissolved in a mixture of methylene chloride (90ml) and methanol (10ml). Argon is bubbled through the solution for 10 minutes. The solution is irradiated using a Rayonnet type system (λ= 254nm) for 3 to 4 hours (TLC control). After complete disappearance of the starting material, the solvent is removed and the crude product is purified by flash-chromatography.

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(9) Its interesting to note that the direct irradiation of ether **3c** in benzene in the presence of small amounts of TsOH leads to 1-indanone. See: Piva, O. *Tetrahedron Lett.* **1992**, 33, 2459.

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