Photochemical Selective Desilylation of *t*-Butyldimethylsilyl Ethers

Mei Zhong JIN, Li YANG, Long Ming WU, You Cheng LIU, Zhong Li LIU*

National Laboratory of Applied Organic Chemistry,
Lanzhou University, Lanzhou 730000

Abstract: A photochemical desilylation reaction with nearly quantitative yield and excellent selectivity between silyl alkyl ether and silyl enol ether is reported.

Keywords: Photoinduced electron transfer, selective desilylation.

The silyl moiety, *e.g.*, trimethylsilyl (TMS), has been widely used as a protecting group for alcohols or aldehydes and ketones in organic synthesis *via* formation of alkyl silyl ethers or enol silyl ethers respectively. Generally, the protecting silyl group was removed by fluoride ion[1], acid[2] or base[3]. However, these deprotection methods afford little selectivity between silyl alkyl ethers and silyl enol ethers. Recently, photochemical approaches of desilylation have also been developed[4-7]. Kochi and coworkers[6] reported that the silyl group in silyl enol ethers could be photochemically removed to afford enones in the presence of equimolar chloranil in acetonitrile or methylene chloride, but the reaction was always accompanied by formation of significant amount of enol-chloranil adducts and the yield of enones was ranging from 5 % - 83 %, depending on the structure of the silyl enol ether and the solvent used. Gassman and Bottorff[7] reported that irradiation of 1-cynaonaphthalene and biphenyl with cyclohexenol trimethylsilyl ether in acetonitrile/methanol mixed solvent (3:2 v/v) produced cyclohexanone, while cyclohexyl trimethylsilyl ether kept intact. Unfortunately, the yield of the cyclohexanone was only *ca*. 60% that was far from satisfactory.

We wish to report herein an improved photochemical approach for effective and selective desilylation of silyl enol ethers in the presence of silyl alkyl ethers. By use of catalytic amount of dichloronaphthaquinone (DCNQ) or chloranil (CA) as the sensitizer and *iso*-propyl alcohol as the solvent *t*-butyldimethylsilyl (TBDMS) enols **1** were converted to ketones **2** with excellent yield upon u.v.-irradiation, while silyl alkyl ether **3** kept intact. The results are summarized in **Scheme 1** and **Table 1**.

In a typical experiment, silyl enol ethers **1** (0.5mmol) and DCNQ (0.025mmol, 5% molar ratio of **1**) was dissolved in 5ml of *iso*-propyl alcohol and the solution was deaerated by bubbling argon for 10 min, then the solution was irradiated with a 500W high pressure mercury lamp in a Pyrex bottle (λ>300 nm). The reaction was monitored by GC and the products were isolated by silica gel column chromatography and identified by NMR and MS spectroscopy. In case of using CA as the sensitizer 5 ml of acetonitrile/*iso*-propyl alcohol mixed solvent (4:1 v/v) was used to facilitate the solubility of CA.

Scheme 1

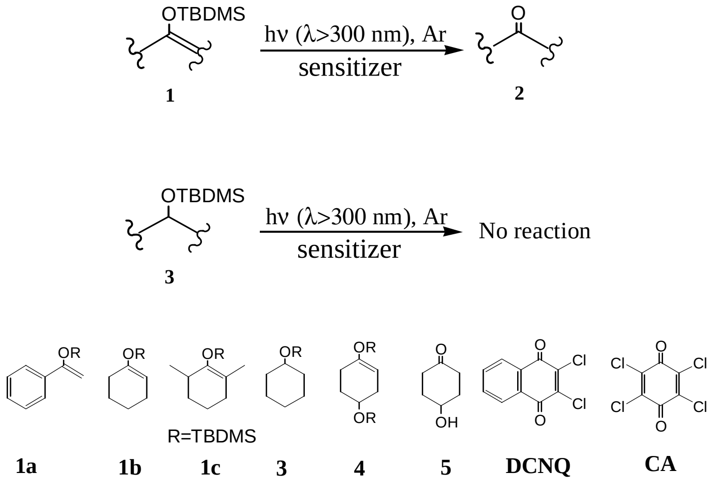
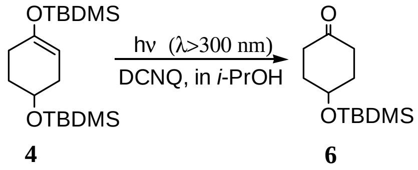


Table 1 Photochemical desiylation of silyl ethers

Substrates	Sensitizer	t/h	Conversions (%)	Yields (%)
1a	CA	1.5	100	92
1a	DCNQ	3.0	100	97
1b	CA	1.5	100	88
1b	DCNQ	3.0	100	94
1c	CA	1.5	100	91
1c	DCNQ	3.0	100	95
3	CA	1.5	5	0
3	DCNQ	3.0	0	0

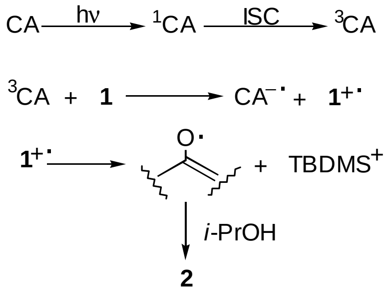
It is seen from **Table 1** that the present approach affords much higher yields than the photochemical desilylation methods reported previously[6,7], making it a synthetically useful reaction. In addition, the silyl alkyl ether **3** was very stable under the experimental conditions that is distinctly different from the conventional desilylation methods[1-3] and makes a selective desilylation possible. Therefore, bifunctional compound **4** was synthesized[8] and subject to photosensitized reaction under the same experimental conditions mentioned above. It was found that after irradiation for 3.5 h **4** was exclusively converted to **6**[9] (conversion 100 %, yield 98 %) and not any **5** could be detected by GC after completion of the reaction (**Scheme 2**).

Scheme 2



In dark control experiments no reaction took place in all of the above mentioned reactions. The oxidation potential of silyl enol ethers are around 1.2-1.5 V *vs*. SCE[6,7] and the reduction potential of chloranil is 0.02 V *vs*. SCE[6]. This makes the photoinduced electron transfer between **1** and chloranil energetically feasible (ΔG = -(88-58) kJ/mol as calculated by using Rehm-Weller equation[10]). Therefore, a photoinduced electron transfer mechanism is proposed as examplified in **Scheme 3**. In the scheme electron transfer between triplet chloranil and **1** produces the corresponding radical cation $\mathbf{1}^{+\cdot}$ and radical anion $CA^{-\cdot}$. It is well known that radical cations are very unstable and easy to subject so-called mesolytic cleavage[11] to fragment, excluding a proton and/or an alkyl cation. It was reported that silyl cation is extremely easy to leave from its radical cation and the fragmentation rate of a silyl cation is over two orders of magnitude faster than a proton from the corresponding radical cation[12]. Therefore, in the present case the silyl cation must preferentially fragment from $\mathbf{1}^{+\cdot}$, leaving the alkoxyl radical. Since *iso*-propyl alcohol which is a very good hydrogen donor[13] was used as the solvent, the alkoxyl radical must preferentially abstract a hydrogen from the solvent to form product **2**, rather than react with CA to form the adduct as reported previously when the reaction was conducted in acetonitrile[6]. The use of catalytic amount of the sensitizer also diminishes the possibility of the addition reaction. The electron transfer can not take place between silyl alkyl ether **3** and CA because the oxidation potential of **3** is approximately 1.0 V higher than **1**[14], making the electron transfer energetically unfavorable.

Scheme 3



In summary, this work affords an effective photochemical deprotecting approach for selective desilylation between silyl enol ethers and silyl alkyl ethers that may be used in synthetic organic chemistry.

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References and notes

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