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3-Trimethylsilyloxy-oxetanes via a Highly Selective Paterno-Büchi Reaction

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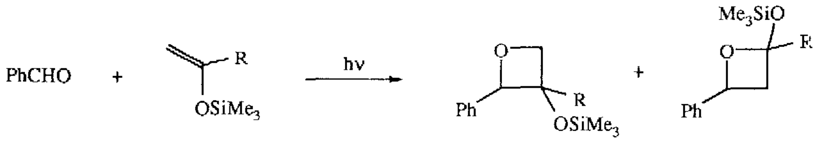
Abstract: Benzaldehyde reacts photochemically with various trimethylsilyl enol ethers to furnish 3-trimethylsilyloxy-oxetanes in moderate to fair yields. The photocycloaddition proceeds with excellent regio- and diastereoselectivity.

The Paterno-Büchi reaction,[2] namely the [2+2]-photoaddition of a carbonyl compound to an olefin, constitutes the simplest and most convenient route to functionalized oxetanes.[3] Both the mechanism and the synthetic scope of the reaction have been extensively studied during the last decades.[4]

Photocycloaddition of enol ethers to aldehydes or ketones provides substituted oxetanes with modest to good regioselectivity leading mainly to the corresponding 3-alkoxy-oxetanes.[5] The regioselectivity can be improved if silyl enol ethers are used as alkenes.[6] In the reaction of furans with aldehydes 2-alkoxy-oxetanes are the major products.[7] Dihydrofurans, however, behave like their acyclic analogs forming the 3-substituted oxetane.[8] The processes involving furans[9] and dihydrofurans[10] occur with high simple diastereoselectivity.

Contrary to that, the Paterno-Büchi reaction of acyclic enol ethers with aldehydes has yet failed to produce oxetanes stereoselectively.[11] We now report that silyl enol ethers show excellent regio- and stereochemical results in their photocycloaddition to benzaldehyde (equation 1). Some illustrative examples are given below.



1 2 3

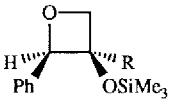
(1)

Table 1. Photocycloaddition of Various Trimethylsilyl Enol Ethers to Benzaldehyde[12]

R	alkene	yield* [%]	2/3**	ds**
Ph	**1a**	39	>95/5	>95/5
t-Bu	**1b**	59	>95/5	93/7
t-BuS	**1c**	27	>95/5	>95/5

* after chromatography, not optimized
** determined by ^{1}H-NMR of the crude product mixture

Reactions were conducted in an inert solvent (hexane or toluene) at 0°C utilizing a 150 W Hg-lamp as irradiation source (pyrex filter).[12] Chemical shift data and NOE experiments are in good agreement with the shown relative configuration for the major diastereoisomer.



R = Ph **2a**
R = t-Bu **2b**

The assignment for **2c** has not been definitely established so far mainly due to the fact that the minor product could neither be isolated nor spectroscopically detected.

From a simplified mechanistic point of view the reaction can be envisaged as an electrophilic attack of the photoexcited aldehyde at the electron rich alkene which leads to formation of the O-C bond. The intermediate biradical collapses to the final product or it cleaves back to the starting materials. This model which is based on the thorough investigations by Freilich and Peters[13] enables to explain both the regio- and stereoselectivity of the reaction. Obviously the ring closure occurs preferentially such that the two large substituents (Phenyl and R) approach each other in an anti-manner.

We believe that the described selective route to 3-trimethylsilyloxy-oxetanes will be of great value for the construction of complex carbon skeletons. Our efforts are currently devoted to the extension of this method to other silylenolethers and aldehydes and its application to natural product synthesis.

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12. *Typical procedure*: 2.85 mmol benzaldehyde (302 mg) and 5.00 mmol 1-t-butyl-1-trimethylsilyloxy-ethene **1b** (860 mg) were dissolved in 50 ml degassed hexane. The mixture was irradiated with a 150 W Hg-lamp (TQ 150, Original Hanau) at 0°C for 1 hour (pyrex-filter). After removal of the solvent the crude product mixture was analyzed NMR spectroscopically and subsequently purified by flash chromatography (Merck silica gel 230-400 mesh ASTM; eluent: petroleum ether/ethyl acetate=10/1). 470 mg (59%) of the analytically pure oxetane **2b** were obtained as a colorless oil.

    All new compounds gave satisfactory elemental analyses and were identified by MS (FD), ^{1}H- and ^{13}C-NMR spectroscopy. ^{1}H-NMR data for the major diastereoisomers (CDCl$_3$, 300 MHz): **2a** -0.20 (s, 9H), 4.98 (d, 1H, J=6.9 Hz), 5.18 (d, 1H, J=6.9 Hz), 5.76 (s, 1H), 7.24-7.47 (m, 8H), 7.54-7.61 (m, 2H). **2b** -0.29 (s, 9H), 1.10 (s, 9H), 4.62 (d, 1H, J=6.9 Hz), 4.69 (d, 1H, J=6.9 Hz), 5.63 (s, 1H), 7.20-7.39 (m, 5H). **2c** 0.00 (s, 9H), 1.46 (s, 9H), 4.72 (d, 1H, ^{2}J=7.1 Hz), 4.95 (dd, 1H, ^{2}J=7.1 Hz, ^{4}J=0.6 Hz), 6.03 (d, 1H, ^{4}J=0.6 Hz), 7.19-7.45 (m, 5H).
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