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Oxyfunctionalization Reactions by Perfluoro *Cis*-2,3-dialkyloxaziridines. Enantioselective Conversion of Silanes into Silanols.

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Abstract: Perfluoro cis-2,3-dialkyloxaziridine **2** is shown to perform the oxyfunctionalization of silanes **1** under very mild conditions to give silanols and silanediols **3** in high chemical yields and complete enantioselectivity.

Perfluoro *cis*-2,3-dialkyloxaziridine **2** performs effectively the oxidation of sulfides to sulfoxides or sulfones,[1a] olefins to epoxides,[1b] alcohols to ketones.[1c] More interesting, unactivated hydrocarbon sites have been hydroxylated cleanly[1d] also in complex polyfunctional compounds of biological interest.[1e]

Silanols are key compounds in organosilicon chemistry[2] and in chiral and non-racemic form they are of interest as a consequence of the high eudismic ratio shown by drugs containing this moiety.[3] Syntheses of silanols require the employment of neutral conditions otherwise condensation to disiloxanes lowers the yields in isolated products. A distinctive feature of perfluorinated oxaziridines is their ability to work as potent yet selective oxidizing species under neutral and aprotic conditions. It became therefore attractive to prove that these oxaziridines can be used for an oxidation of silanes to silanols which is both enantioselective and preparatively useful.

Specifically, silanes **1a-h** afford corresponding silanols **3a-h** when treated with equimolar amounts of perfluoro *cis*-2-*n*-butyl-3-*n*-propyloxaziridine **2**, perfluoro azaalkene **4** being the only co-product formed in the oxidation.[4] Alkyl, aryl, alkenyl, and alkynyl residues can be present on silicon and yields are invariably high (Table 1).[5] Also geminal dihydroxylation of a SiH_2 group can be performed and yield in corresponding silanediol is nearly quantitative (compound **1i**). Apolar ($CFCl_3$, $CHCl_3$, CH_2Cl_2, $CFCl_2CF_2Cl$) or protic (CF_3CH_2OH, $(CF_3)_2CHOH$) solvents can be used interchangeably. Reactions are retarded by steric hindrance around silicon (for instance, *tri-n*-octylsilane **1b** reacts slower than *tri*-ethylsilane **1a**), they occur nearly instantaneously at room temperature, but require one to two hours to go to completion at -78 °C.[6] Oxyfunctionalization of (+)-(*R*)-methyl-α-naphthyl-phenylsilane (**1h**)[7] affords corresponding silanol **3h** having the (+)-(*S*) configuration and at room temperature and in $CFCl_3$ solution the reaction occurs with complete retention of configuration.[8] Other oxidizing agents with a reactivity recalling that of oxaziridine **2**

Table 1. Oxidation of Silanes **1** to Silanols **3**.

Compound	R^1	R^2	R^3	Yield %
1a	C_2H_5	C_2H_5	C_2H_5	>95
1b	n-C_8H_{17}	n-C_8H_{17}	n-C_8H_{17}	>95
1c	C_6H_5	C_6H_5	C_6H_5	>95
1d	$CH_2C_6H_5$	CH_3	CH_3	>95
1e	$C_6H_4SiH(CH_3)_2$	CH_3	CH_3	>95[a]
1f	$C_6H_5C{\equiv}C$	CH_3	CH_3	90
1g	$CH_2{=}CHCH_2$	CH_3	CH_3	88[b]
1h	CH_3	C_6H_5	α-$C_{10}H_7$	>95
1i	C_6H_5	C_6H_5	H	>95[c]

[a]Yield is referred to dimethyl-(4-dimethylhydroxysilyl)phenylsilanol. [b]Yield is referred to dimethyl-2,3-epoxypropylsilanol. [c]Yield is referred to diphenylsilanediol.

have been used in similar oxyfunctionalization processes.[7,9]

In conclusion, a new approach for the enantiospecific and direct oxidation of silanes to silanols is described. The preparative value of the methodology is due to the fact that oxaziridine **2** is easily available in large quantities, reaction conditions are notably mild, a wide range of solvents can be employed for the reaction, the work-up procedure is remarkably simple.

References and Notes

1. (a) DesMarteau, D. D.; Petrov, V. A.; Montanari, V.; Pregnolato, M.; Resnati, G. *J. Org. Chem.* in press. (b) Petrov, V. A.; Montanari, V.; Resnati, G.; DesMarteau, D.D. *J. Fluorine Chem.* **1991**, *33*, 399. (c) DesMarteau, D. D.; Petrov, V. A.; Montanari, V.; Pregnolato, M.; Resnati, G. *Tetrahedron Lett.* **1992**, *33*, 7245. (d) DesMarteau, D. D.; Donadelli, A.; Montanari, V.; Petrov, V. A.; Resnati, G. *J. Am. Chem. Soc.* **1993**, *115*, 4897. (e) Arnone, A.; Cavicchioli, M.; Montanari, V.; Resnati, G. *J. Org. Chem.* submitted.
2. Armitage, D. A. *Organosilanes*, in: *Comprehensive Organometallic Chemistry*; Wilkinson G.; Stone, F. G. A.; Abel E. W. Eds.; Pergamon Press: Oxford, 1982; pp. 1-204.
3. Tacke, R.; Zilch, H. *L'Actualité Chimique* **1986**, *(3)*, 75. Tacke, R.; Linoh, H.; Ernst, L.; Moser, U.; Mutschler, E.; Sarge, S.; Cammenga, H. K.; Lambrecht, G. *Chem. Ber.* **1987**, *120*, 1229.
4. Reactions were monitored through TLC, GC, ^1H and ^{19}F NMR. When no more starting material was present, the reaction mixture was diluted with methylene chloride and washed twice with perfluoro *tri-n*-butylamine in order to remove azaalkene **4**. Evaporation of the solvent from the residue afforded silanols **3** in nearly pure form. Expected IR, ^1H NMR, and mass spectra were obtained.
5. When allyldimethylsilane **1g** is treated with one equivalent of oxaziridine **2**, dimethyl-2,3-epoxypropylsilane is main reaction product thus showing that epoxidation of the double bond is easier than oxyfunctionalization at silicon. On addition of a second equivalent of the oxaziridine, dimethyl-2,3-epoxypropylsilanol forms cleanly.
6. Oxyfunctionalization of silanes occurs under milder conditions than oxyfunctionalization of hydrocarbons (refs. 1d,e). Furthermore, while oxidation of a SiH_2 group is performed easily, oxidation of a CH_2 has never been observed. This is probably related to the fact that Si-H bonds are weaker than C-H bonds.
7. Sommer, L. H.; Frye, C. L.; Parker, G. A.; Michael, K. W. *J. Am. Chem. Soc.* **1964**, *86*, 3271.
8. Enantiomeric excesses of (+)-(*R*)-**1g** and of the formed (+)-(*S*)-**3g** were shown to be >98.5 through HPLC analyses (Chiralcel OD, Daicel Chemical Industries, LTD) and ^1H NMR analyses with Eu(hfc)$_3$. Interestingly, when the reaction is performed at -78 or -20 °C, the oxidation still occurs with retention of configuration, but a lower enantioselectivity is observed (e. e. 45-66%).
9. Adam, W.; Mello, R.; Curci, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 890.

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