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A SHORT AND GENERAL SYNTHESIS OF α-KETOACYLSILANES

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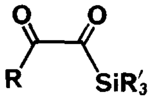
Abstract: α-Ketoacylsilanes may be prepared by the sequential osmium tetroxide catalysed dihydroxylation and Swern oxidation of <u>cis</u>-vinylsilanes. Addition of nucleophiles to α-ketoacylsilanes occurs to give products arising exclusively from reactions at the silicon-bearing carbonyl group.

As a part of our continuing interest in acylsilane chemistry[1] we required a general preparative method for α-ketoacylsilanes (1). Reich[2] has reported the isolation of α-ketoacylsilane (2) by epoxidation and rearrangement of allene (3), however this procedure does not allow the preparation of α-ketoacylsilanes which do not possess β-hydrogen atoms.



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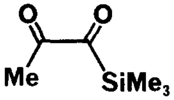

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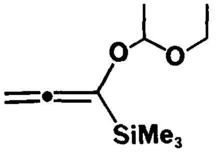

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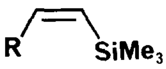

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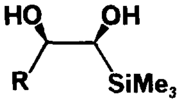
We have found that, in accordance with a recent report by Hudrlik[3], the osmium tetroxide catalysed oxidation of <u>cis</u>-vinyltrimethylsilanes (4)[‡] occurs to give the corresponding erythro-1,2-diols (5) in reasonable yields when trimethylamine-N-oxide is used as reoxidant. Use of alternative reoxidants such as t-butylhydroperoxide results in the formation of aldehydes (6) and silyl enol ethers (7) as the sole products[4].



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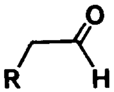

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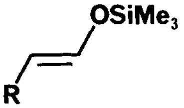

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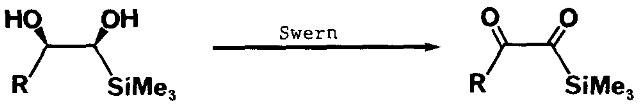
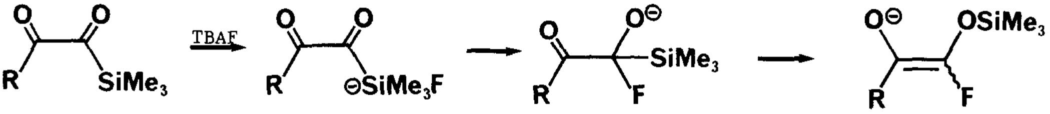
Pyridinium chlorochromate oxidation of diol (5, R=Ph) gave only aldehyde (6, R=Ph) in excellent yield (90%), presumably by electrofugal loss of the silicon moiety; however, use of the Swern procedure[5] ($(COCl)_2$, DMSO, CH_2Cl_2 , -60 C) allowed isolation of the light-sensitive deep crimson α-ketoacylsilanes (1, R'=Me) from diols (5) in acceptable yields. Purification was conducted by dry flash column chromatography on silica gel (Merck 15111) at -78 C in the dark or by vacuum distillation in the dark. α-Ketoacylsilanes show two signals in their infra-red absorption spectra corresponding to the two carbonyl groups, typically at 1680-1715 and 1600-1650 cm-1 (acylsilane).



R=Ph	55%
$^{n}C_5H_{11}$	39%
$^{n}C_4H_9$	41%



Scheme

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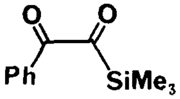
α-Ketoacyltrimethylsilanes undergo smooth protiodesilylation using tetra-n-butylammonium fluoride (TBAF) in thf/0.1M HCl (20:1) to provide α-ketoaldehydes in moderate yields (Scheme). This reaction probably proceeds by nucleophilic attack of fluoride ion at the electropositive silicon atom followed by rearrangement and silyl migration to give enolate (8), a mechanism first suggested by Brook[6]. Protic quench and loss of trimethylsilylfluoride would then give α-ketoaldehydes. Upon treatment with osmium tetroxide/ t-butylhydroperoxide in anhydrous methanolic solution benzoylacyltrimethylsilane (9) yields methyl phenylglyoxylate (10, 45%), presumably by a parallel process in which a solvent molecule acts as the nucleophile. Subsequent in situ oxidation of the resulting ketoaldehyde or silyl ether would provide the observed α-ketoester product. We have recently reported the reaction of silylacetylenes with osmium tetroxide under similar conditions to produce α-ketoesters in good yields[1] and we believe that α-ketoacylsilanes are intermediates in the transformation. Treatment of acetylacylsilane (2) with sodium borohydride in methanol at -78 C also results in reaction at the more electrophilic silicon-bearing carbonyl group to give the α-hydroxy-α-silylketone (11) as the only isolable product (41%).



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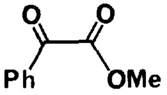

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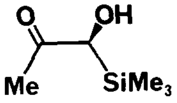

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‡ Prepared by the diisobutylaluminium hydride reduction of trimethylsilylacetylenes under conditions of kinetic control.

References

1. P. C. B. Page and S. Rosenthal, Tetrahedron Lett., 1986, in press.
2. H. J. Reich, M. J. Kelly, R. E. Olson, and R. C. Holtan, Tetrahedron, 1983, **39**, 949.
3. P. F. Hudrlik, A. M. Hudrlik, and A. K. Kulkarin, J. Am. Chem. Soc., 1985, **107**, 4260.
4. G. Stork and E. Colvin, J. Am. Chem. Soc., 1971, **93**, 2080.
5. D. Swern, D. S. Brownfain, and A. J. Mancuso, J. Org. Chem., 1979, **44**, 4148; R. E. Ireland and D. W. Norbeck, J. Org. Chem., 1985, **50**, 2198.
6. A. G. Brook and N. V. Schwartz, J. Org. Chem., 1962, **27**, 2311.

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