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THE SILAPINACOL REARRANGEMENT: CONVERSION OF α,β-DIHYDROXYSILANES INTO α-SILYL CARBONYL COMPOUNDS

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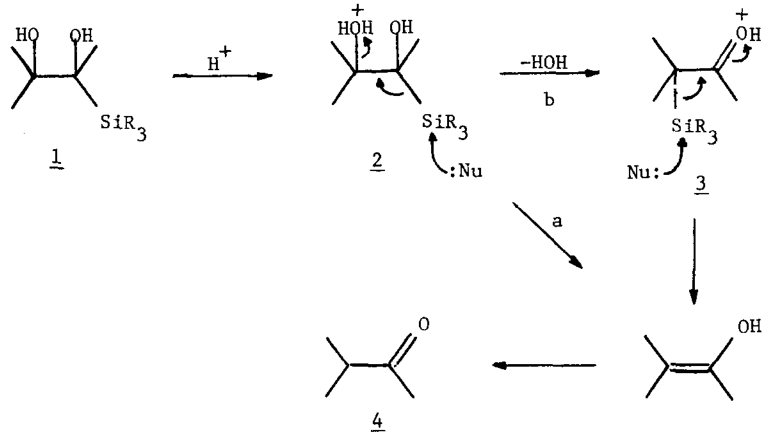
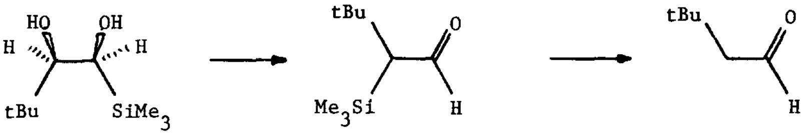
Summary: Treatment of α,β-dihydroxysilanes with trifluoroacetic acid in chloroform results in a 1,2-migration of the silyl group to give α-silyl aldehydes and ketones. The *t*-butyldimethylsilyl compounds can be isolated in high yields.

Several workers[1] have reported that α,β-dihydroxytrimethylsilanes (1, R = Me) are converted to desilylated carbonyl compounds (4) under the influence of protonic acids, a process which has generally been considered to proceed via β-elimination (path a) of a protonated intermediate (2). We wish to present evidence that, at least under certain conditions, this process instead follows the sequence indicated by path b, wherein loss of water from the beta-site is accompanied[2] by a 1,2-silyl group migration ("silapinacol rearrangement")[3] to afford the intermediate 3. This may then suffer subsequent desilylation to generate the observed carbonyl compound 4.[4]



Evidence for the participation of 3 in this process was first afforded by extended-time examination of a ^{1}H NMR sample ($CDCl_3$) of diol 5.[5] Within 0.5 h at 25°C, absorptions attributed to 6[6] appeared, coexisting with those of 5 for some hours, but slowly diminishing over a one day period in favor of absorptions due to 7.[7]



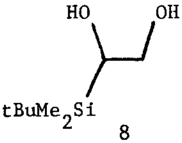
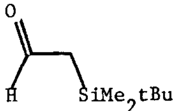
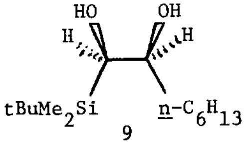
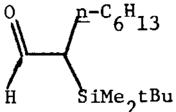
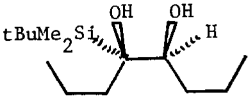
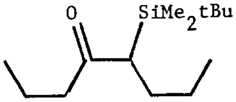
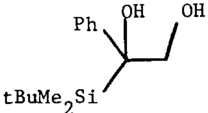
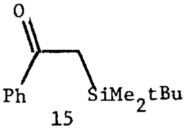
5 6 7

On the assumption that both rearrangement and desilylation were being catalyzed by traces of HCl in the chloroform, conditions expected to accelerate the former but retard the latter process were chosen for further investigation. Thus a series of α,β-dihydroxysilanes containing the more sterically hindered t-butyldimethylsilyl group (8-11) was prepared by osmium tetroxide-catalyzed dihydroxylation[1d] of the appropriate t-butyldimethylsilyl alkenes.[8] These diols were then subjected to treatment with trifluoroacetic acid in chloroform under initially anhydrous conditions[9] to afford high yields of α-silyl carbonyl compounds 12-15.

A typical procedure consisted of treating 50-100 mg of diol in 2 ml of chloroform with the indicated amount of trifluoroacetic acid. After NMR analysis indicated the absence of starting diol, sufficient $KHCO_3$ to neutralize the acid was added, the solution filtered through anhydrous $MgSO_4$, concentrated and Kugelrohr distilled.[10] Results are displayed in Table 1.

In contrast to asilyl systems,[3] we have as yet seen no products arising from alkyl or hydride migration to incipient carbocationic sites. Notable in this regard is diol 11, which does not undego either a 1,2-phenyl group shift or diversion to products expected from potential generation of a tertiary, benzylic carbocation. Thus, silyl group migration dominates the chemistry of these species. Other notable features of the method are its simplicity, high yields of products, the structural variations allowed, and the ability to generate both α-silyl aldehydes and ketones from, ultimately, alkenylsilanes.[11] Such carbonyl compounds are of utility as alkenyl cation equivalents,[12] and α-silyl aldehydes in particular are few in number and have heretofore generally been available only by more circuitous routes.[4a,12,13]

TABLE 1. α-SILYL CARBONYL COMPOUNDS FROM α,β-DIHYDROXYSILANES[a]

DIOL	CONDITIONS[b]	PRODUCT	YIELD[c] (%)
 8	1:1, 25h	 12	85[d,e]
 9	10:1, 18h	 13	86[e]
 10	4:1, 2h	 14	90
 11	1:2, 19h	 15	99

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[a] Combustion, MS, IR and ^{1}H NMR data consistent with all new structures was obtained.

[b] Mole ratio of diol : CF_3CO_2H, respectively. Conditions not optimized.

[c] Isolated from Kugelrohr distillation.

[d] Corrected for ca. 9% of impurity showing 1795 cm^{-1} IR absorption.

[e] Compound previously reported in ref. 4a.

REFERENCES AND NOTES

1. (a) C.M. Robbins, G.H. Whitham, *Chem. Commun.*, 697 (1976). (b) P.F. Hudrlik, J.P. Arcoleo, R.H. Schwartz, R.N. Misra, R.J. Rona, *Tetrahedron Lett.*, 591 (1977). (c) A.P. Davis, G.J. Hughes, P.R. Lowndes, C.M. Robbins, E.J. Thomas, G.H. Whitham, *J. Chem. Soc.*, *Perkin Trans. 1*, 1934 (1981). (d) P.F. Hudrlik, A.M. Hudrlik, A.K. Kulkarni, *J. Am. Chem. Soc.*, **107**, 4260 (1985).
2. We have no evidence as to whether these are concerted or stepwise phenomena.
3. Pinacol rearrangement review: C.J. Collins, *Quart. Rev. Chem. Soc.*, **14**, 357 (1960).
4. α-Silyl carbonyl compounds are known to be sensitive to protonic desilylation. See (a) P.F. Hudrlik and A.K. Kulkarni, *J. Am. Chem. Soc.*, **103**, 6251 (1981). (b) G.L. Larson, D. Hernandez, I. Montes de Lopez-Cepero, L.E. Torres, *J. Org. Chem.*, **50**, 5260 (1985).
5. **5**: ^{1}H NMR ($CDCl_3$, $CHCl_3$ taken as δ 7.26) δ 0.11 (s, 9H), 0.97 (s, 9H), 1.33 (broad s, 2H), 3.49 (AB pattern, J = 7.7 Hz, 2H); IR 3500 (sh), 3400, 1245, 835 cm^{-1}.
6. **6**: ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 9H), 1.11 (s, 9H), 2.09 (d, J = 5.9 Hz, 1H), 9.70 (d, J = 5.9 Hz, 1H).
7. P.L. Bock, D.J. Boschetto, J.R. Rasmussen, J.P. Demers, G.M. Whitesides, *J. Am. Chem. Soc.*, **96**, 2814 (1974); G.J. Karabatsos, N. Hsi, *J. Am. Chem. Soc.*, **87**, 2864 (1965).
8. Synthesized by using *t*-butyldimethylsilyl (TBDMS) reagents in standard approaches: TBDMS ethene from TBDMS fluoride and vinyllithium; *Z*-1-TBDMS-1-octene from (a) 1-TBDMS octyne and diisobutylaluminum hydride (b) H_3O^+ [R.B. Miller, G. McGarvey, *J. Org. Chem.*, **43**, 4424 (1978)]; *E*-4-TBDMS-4-octene from TBDMS hydride and 4-octyne, H_2PtCl_6; 1-phenyl-1-TBDMS ethene from (a) 1-phenyl-2-trimethylsilylethyne and TBDMS hydride, H_2PtCl_6 (b) CF_3CO_2H [P.F. Hudrlik, R.H. Schwartz, J.C. Hogan, *J. Org. Chem.*, **44**, 155 (1979)]. All alkenes are new compounds and displayed appropriate spectral and analytical data.
9. A second phase, presumably water, was seen to separate during most runs.
10. Material thus obtained was generally 90-95% pure by NMR analysis, but showed varying amounts of IR absorption at 1795 cm^{-1} ($CF_3C{=}O$?).
11. We have preliminary evidence that silyl epoxides, also directly obtainable from alkenylsilanes, undergo protonolysis to α-silyl carbonyl compounds.[14] Thus, treatment of *cis*-1-TBDMS-2-*n*-hexyloxirane with CF_3CO_2H in chloroform affords **13**.
12. (a) G.L. Larson, α-Silyl Carbonyl Compounds: Synthesis and Reactions" in *Silicon Compounds; Register and Review*, Petrarch Systems, Inc., Bristol, Pennsylvania (USA), 1984. (b) Ref. 4a.
13. L. Birkhofer and W. Quittmann, *Chem. Ber.*, **118**, 2874 (1985).
14. For a previous example of this behavior (in part), see J.J. Eisch and J.E. Galle, *J. Org. Chem.*, **41**, 2615 (1976).

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