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α-Alkoxystannanes as masked oxonium ions: application to the synthesis of furo[2,3-*b*]pyrans

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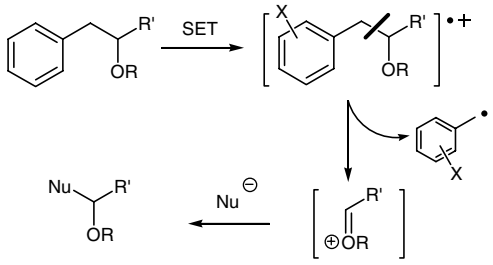
Abstract—α-Alkoxystannanes undergo oxidation upon treatment with cerium ammonium nitrate generating oxonium ions, which can be trapped in an intramolecular fashion affording furo[2,3-*b*]pyrans.

The generation and interception of oxonium (oxacarbenium) and iminium ions play a pivotal role in many synthetic and biological processes.[1] Although these reactions have broad synthetic utility, there are cases where functionality sensitive to Lewis acids necessitates the development of alternate methods for oxonium ion generation. An attractive alternative to this scenario involves the use of SET reactions.[2] Here the key step involves fragmentation of a radical cation to a carbenium ion and a stable radical, for example, Scheme 1, sequences which have been realized both in solution[3] and supported phases.[4]



Scheme 1. SET approach to oxonium ion generation.[3]

The oxidation of organometallic species has been studied extensively[5] and given our interest[6,7] in the use of α-alkoxystannanes in synthesis we were aware of the seminal investigations from Yoshida's[8] group concerning the electrochemical oxidation of group 14 organometallics. These workers have demonstrated that the oxidation potential of α-heterosubstituted organosilanes and organostannanes are significantly reduced due to a $\sigma_{M\text{-}C}$–n_X interaction such that their oxidation in solution becomes relatively facile (Fig. 1).

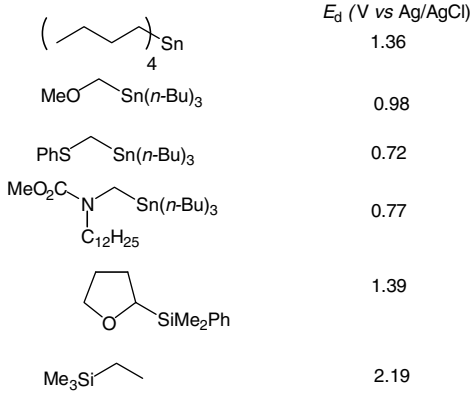


Figure 1. Decomposition potentials of organostannanes/silanes.[11]

Keywords: SET; CAN; Stannane; Oxidation; Oxonium; Acetal.
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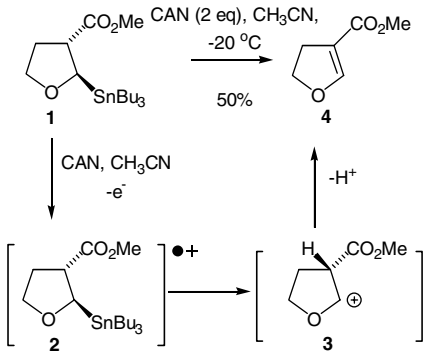
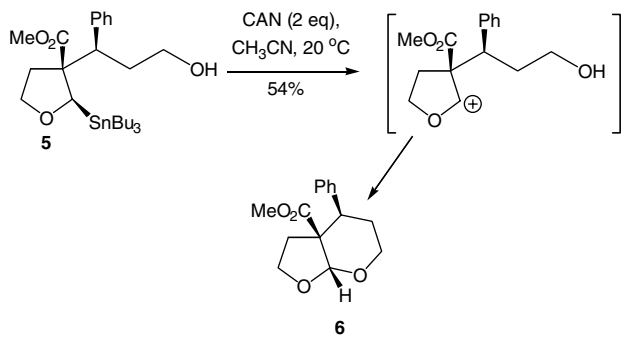


Scheme 2. Oxidative destannylation using CAN.

In earlier work,[7] we demonstrated that SET fragmentation[9] of α-alkoxysilanes could also be effected by chemical oxidants such as CAN,[10] albeit under relatively forcing conditions (CAN, AcOH, 70 °C), thereby providing an alternate to Yoshida's electrochemical procedures.[11] The electrochemical data suggest that oxidation of the analogous α-alkoxystannanes should be more facile (Fig. 1) and it was with this thought in mind that the oxidation of the readily available stannane **1** was undertaken.

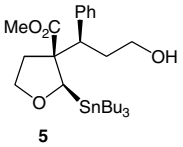
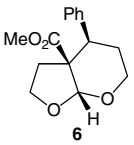
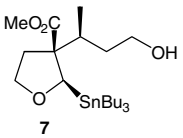
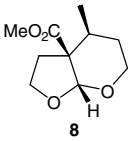
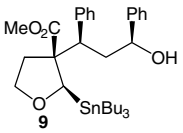
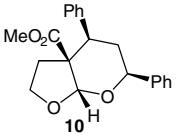
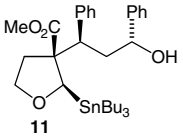
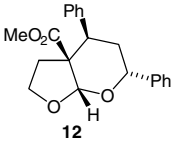
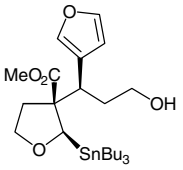
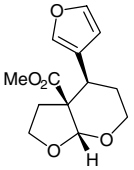
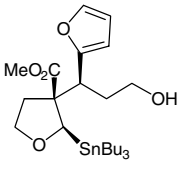
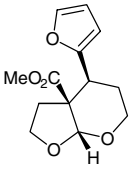
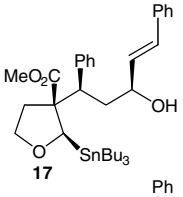
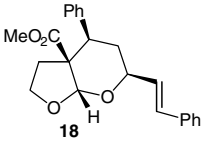
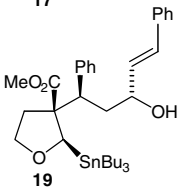
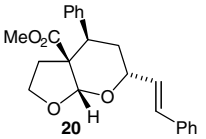
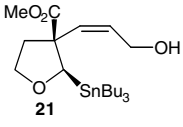
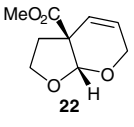
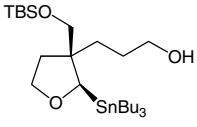
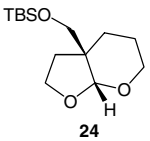
The exposure of **1** to CAN (2 equiv, 20 °C) in dry acetonitrile afforded the unsaturated ester **4** in 50% yield. We reasoned that **4** arose via the intermediacy of the oxonium ion **3**, which itself is the product of SET oxidation of **1** to the radical cation **2** followed by fragmentation. In this instance, the oxonium ion **3** collapses to **4** by proton loss rather than suffering an interception with the solvent (Ritter[12] reaction). We concluded that incorporation of a nucleophilic centre at C3 into these substrates would enhance the likelihood of oxonium ion capture.[7] Gratifyingly, exposure of the stannane **5**[13] to CAN in acetonitrile, as above, resulted in the disappearance of starting material (TLC; 45 min) and ultimately afforded the bicyclic acetal **6** in 54% isolated yield (Scheme 3).

We have subsequently shown that this SET-intramolecular capture sequence is relatively general (Table 1) leading to the synthesis of functionalized furo[2.3-*b*]pyrans[14] in moderate to good overall yields. Whilst CAN performs admirably in such reactions, the use of other single electron oxidants (e.g., $[Fe(Cp)_2]PF_6$) failed to



Scheme 3. Intramolecular oxonium capture.

Table 1. CAN-mediated oxidative acetal forming reactions

Entry	Substrate[a]	Product[a]	Yield (%)
1	 **5**	 **6**	54
2	 **7**	 **8**	74
3	 **9**	 **10**	67
4	 **11**	 **12**	68
5	 **13**	 **14**	86
6	 **15**	 **16**	54
7	 **17**	 **18**	30
8	 **19**	 **20**	27
9	 **21**	 **22**	0[b]
10	 **23**	 **24**	53

[a] All compounds are racemic.
[b] Complex mixture of products.

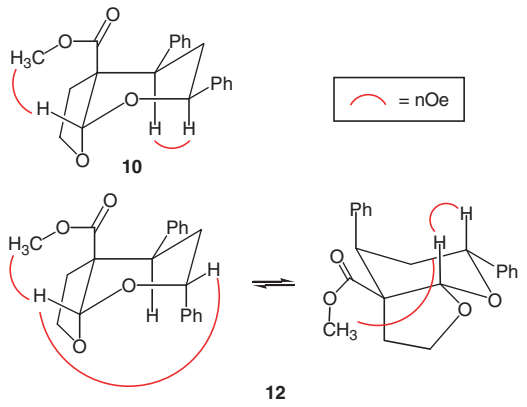


Figure 2. Stereochemical assignments.

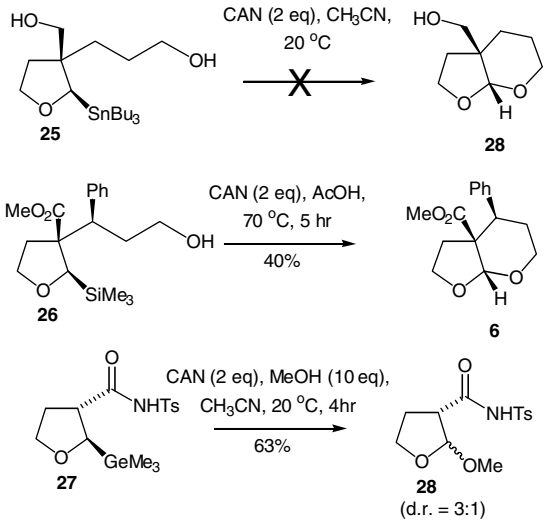
promote the initial SET, presumably due to a mismatching of redox potentials.[15] The stereochemical outcome of these cyclization reactions has been probed using NOE difference techniques, as in the case of **10** and **12** (Fig. 2), the results of which indicate that cis-fused products are produced in each case (Fig. 2).

The oxidation of α-alkoxystannanes obviously proceeds under very mild conditions and is tolerant of a number of common functional groups including ester (entries 1–8), electron-rich aromatics[16] (entries 5 and 6) and TBS-protected alcohol functionality (entry 10). Notably, the cyclization of allylic alcohols does not proceed well (entries 7–9). Curiously diol **25** also appears to be wholly uncreative towards CAN.[9b]

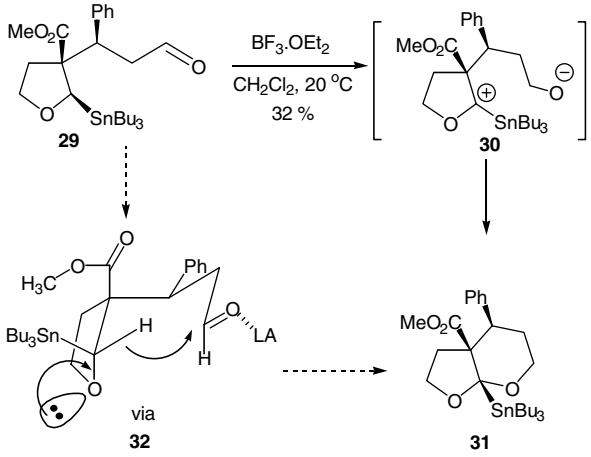
The ease in which stannanes such as **5** undergo this SET-fragmentation reaction should be compared to our earlier study concerning the oxidation of the silane **26**.[7] Here we found that oxidation of silane **26** with CAN proceeded slowly in acetonitrile and was best conducted in acetic acid at 70 °C. Under these conditions, the acetal **6** could be isolated in somewhat diminished isolated yields (40%). Furthermore whilst the carbenium **3**, derived from **1**, could not be captured by the solvent acetonitrile, dissolution of the germane **27**[13] in acetonitrile containing methanol (10 equiv) followed by the addition of CAN (2 equiv) at 20 °C for 4 h resulted in the isolation of **28**, as a 3:1 mixture of diastereoisomers, in 63% yield.[17]

On a purely qualitative basis, the results depicted in Schemes 3 and 4 infer that the reactivity of the germane **27** towards oxidation lies somewhere between that of the silane **26** and the stannane **5** and is a trend which correlates with the available oxidation potential data listed in Figure 1, (i.e., ease of oxidation C–Sn bond > C–Ge bond > C–Si bond).

Finally, we have also observed that exposure of aldehyde **29** to a Lewis acid (e.g., $BF_3{\cdot}OEt_2$) results in the isolation of acetal **31**[18] in which the tin moiety is retained. Presumably, generation of the oxonium ion **30** in this case proceeds via a 1,5-hydride shift,[19] as depicted below (cf. **32**, Scheme 5).



Scheme 4. Oxidation of related organometallics.



Scheme 5. Generation of oxonium ions via a 1,5-H shift.

In conclusion, we have demonstrated that α-alkoxystannanes undergo SET oxidation–fragmentation reactions or 1,5-hydride shifts generating oxonium ions which can be trapped by a pendant alcohol moiety resulting in the isolation of a variety of furo[2,3-*b*]pyrans. Synthetic applications of this methodology will be the focus of future investigations.

Acknowledgements

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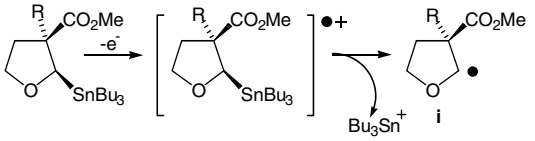

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13. The synthesis of this series of compounds will be reported elsewhere. Typical experimental procedure: preparation of **6**; ceric ammonium nitrate (530 mg, 0.97 mmol) was dissolved in acetonitrile (10 mL). To this mixture was added stannane **5** (255 mg, 0.46 mmol) and the reaction mixture stirred for 45 min. The reaction mixture was added to 1 M sodium carbonate soln. (10 mL). The product was extracted with ether (15 mL × 3) and the combined organic extracts were dried ($MgSO_4$). The solvent was removed in vacuo and the crude product was purified by flash column chromatography (8:2 pet. ether 40–60, EtOAc) to give 89 mg (74%) of the *title compound* **6** as an amorphous white solid. R_f (8:2 pet. ether 40–60, EtOAc) = 0.15; mp 94–95 °C; ν_{max} (film), 2886 (w), 1728 (s) cm^{-1}; δ_H (300 MHz, $CDCl_3$), 7.30 (3H, m, Ar), 7.20 (2H, m, Ar), 5.45 (1H, s, OC*H*O), 4.20 (1H, m, C*H*HO), 4.00 (3H, m, CH*H*O, CH_2O), 3.55 (3H, s, CO_2CH_3), 3.10 (1H, dd $J = 4.0$, 11.5 Hz, C*H*Ph), 2.50 (2H, m, C*H*H–CHPh, C*H*H–CH_2O), 2.25 (1H, m, CH*H*–CH_2O), 1.75 (1H, m, CH*H*–CHPh); δ_C (75 MHz, $CDCl_3$), 172.1 (CO_2Me), 140.6 (Ar), 128.4 (Ar), 128.3 (Ar), 127.4 (Ar), 101.8 (C-1), 64.5 (C-3), 61.3 (C-8), 54.4 (C-5), 51.7 (OCH_3), 43.8 (C-6), 31.9 (C-4), 26.2 (C-7); *m/z* (CI, NH_3), 280 ($[M+NH_4]^+$, 100%); HRMS $C_{15}H_{22}NO_4$ requires 280.1549; found: 280.1550; Anal. $C_{15}H_{18}O_4$ requires C, 68.69%; H, 6.92%; found C, 68.89%; H, 7.16%. Representative spectroscopic data for remaining products: **8** ν_{max} (film) 2957 (w), 2886 (w), 1729 (s), 1455 (w), 1434 (w), 1252 (m), 1208 (m), 1147 (w), 1118 (w), 1100 (w), 1050 (m) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 1.02 (3H, d, $J = 7.0$ Hz, CH_3–CH), 1.65–1.75 (1H, m, OCH$_2$–C*H*H), 1.95–2.05 (1H, m, OCH$_2$–C*H*H), 2.14 (2H, ddd, $J = 5.0$, 8.0, 13.0 Hz, OCH$_2$–C*H*H), 2.49 (1H, ddd, $J = 7.5$, 8.5, 13.0 Hz, OCH$_2$–C*H*H), 3.70–3.80 (1H, m, OC*H*H–CH$_2$), 3.76 (3H, s, CO_2Me), 3.85–3.98 (2H, m, 2 × OC*H*H–CH$_2$), 4.05 (1H, apparent q, $J = 8.0$ Hz, OC*H*H–CH$_2$), 5.18 (1H, s, OC*H*O); δ_C (75 MHz, $CDCl_3$) 17.2, 28.1, 31.6, 31.9, 51.9, 53.9, 56.48, 64.7, 100.8, 173.1; *m/z* (CI) 218 ($[M+NH_4]^+$, 75%), 201 (MH^+, 100%), 185 ($[M-Me]^+$, 20%), 169 ($[M-OMe]^+$, 25%); HRMS $C_{10}H_{17}O_4$ ($[M+H]^+$) requires 201.1127; found 201.1123; **10** ν_{max} (film) 2950 (w), 2893 (w), 1727 (s), 1454 (w), 1210 (m), 1056 (m) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 1.95 (1H, dt, $J = 3.0$, 14.0 Hz, C*H*H–CHPh), 2.27–2.37 (1H, m, OCH$_2$–C*H*H), 2.45–2.57 (1H, m, OCH$_2$–CH*H*), 2.57 (1H, apparent q, $J = 13.0$ Hz, C*H*H–CHPh), 3.25 (1H, dd, $J = 3.5$, 13.5 Hz, OCHPh–CH$_2$–C*H*Ph), 3.60 (3H, s, CO_2Me), 4.10 (1H, dt, $J = 3.5$, 11.5 Hz, OC*H*H–CH$_2$), 4.32 (1H, apparent q, $J = 10.0$ Hz, OCH*H*–CH$_2$), 5.15 (1H, dd, $J = 3.0$,

12.0 Hz, OC*H*Ph), 5.57 (1H, s, OC*H*O), 7.20–7.55 (10H, m, Ar); δ_C (50 MHz, $CDCl_3$) 31.6, 34.5, 44.5, 52.3, 53.1, 64.2, 73.7, 103.1, 126.8, 128.2, 128.2, 128.9, 140.5, 142.2, 172.1; *m/z* (CI) 356 ($[M+NH_4]^+$, 19%), 339 ($[M+H]^+$, 29%), 193 (80%), 188 (100%); HRMS $C_{21}H_{22}O_4$ requires 338.1518; found 338.1525; **12** ν_{max} (film) 2948 (w), 2893 (w), 1733 (s), 1452 (m), 1046 (s) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.10–2.21 (1H, m, CHPh–C*H*H), 2.39–2.51 (2H, m, CHPh–C*H*H, OCH_2–C*H*H), 2.65–2.75 (1H, m, OCH_2–CH*H*), 3.40 (3H, s, CO_2*Me*), 3.50 (1H, dd, $J = 5.0$, 7.0 Hz, C*H*Ph–CH_2), 3.97 (1H, q, $J = 6.0$ Hz, OC*H*H–CH_2), 4.32 (1H, dt, $J = 4.0$, 8.5 Hz, OCH*H*–CH_2), 5.12 (1H, dd, $J = 6.0$, 8.0 Hz, OC*H*Ph), 5.75 (1H, s, OC*H*O), 7.25–7.43 (10H, m, Ar); δ_C (75 MHz, $CDCl_3$) 33.3, 34.0, 44.4, 51.8, 58.6, 67.1, 72.1, 102.6, 125.7, 127.1, 127.5, 128.3, 128.4, 128.5, 141.1, 142.2, 173.0; *m/z* (CI) 356 ($[M+NH_4]^+$, 28%), 339 ($[M+H]^+$, 29%), 210 (40%), 193 (100%); HRMS $C_{21}H_{22}O_4$ requires 338.1518; found 338.1525; **14** ν_{max} (film) 2954 (w), 2887 (w), 1729 (s), 1256 (m), 1208 (m), 1048 (m), 1027 (m) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 1.8–1.9 (1H, m, OCH_2–C*H*H) 2.15–2.37 (2H, m, $2 \times OCH_2$–C*H*H) 2.58 (1H, dt, $J = 8.0$, 12.5 Hz, OCH_2–C*H*H), 3.05 (1H, dd, $J = 5.0$, 11.0 Hz, C*H*-(3-furyl)), 3.55 (3H, s, CO_2*Me*), 3.93 (1H, dt $J = 4.5$, 12.0 Hz, OC*H*H–CH_2), 3.95–4.08 (2H, m, $2 \times$ OC*H*H–CH_2), 4.15 (1H, apparent q, $J = 8.0$ Hz, OC*H*H–CH_2), 5.37 (1H, s, OC*H*O), 6.31 (1H, s, br, OCH=C*H*), 7.32 (1H, s, br, OC*H*), 7.39 (1H, s, br, OC*H*); δ_C (50 MHz, $CDCl_3$) 27.1, 32.8, 34.9, 52.4, 54.1, 61.3, 65.0, 101.9, 110.7, 125.2, 140.1, 143.4, 172.9; *m/z* (CI) 270 ($[M+NH_4]^+$, 100%), 253 ($[M+H]^+$, 18%); HRMS $C_{13}H_{17}O_5$ ($[M+H]^+$) requires 253.1076; found 253.1077; **16** ν_{max} (film) 2952 (w), 2891 (w), 1730 (m), 1208 (m) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 1.89–1.97 (1H, m, OCH_2–C*H*H), 2.17–2.30 (1H, m, OCH_2–C*H*H), 2.40–2.50 (1H, m, OCH_2–C*H*H), 2.51–2.61 (1H, m, OCH_2–C*H*H), 3.30 (1H, dd, $J = 5.0$, 10.0 Hz, C*H*-(2-furyl)), 3.57 (3H, s, CO_2*Me*), 3.97–4.05 (3H, m, $3 \times$ OC*H*H–CH_2), 4.17 (1H, apparent q, $J = 8.0$ Hz, OC*H*H–CH_2), 5.40 (1H, s, OC*H*O), 6.10 (1H, d, $J = 3.0$ Hz, OCH=CH–C*H*), 6.31 (1H, dd, $J = 1.5$, 3.0 Hz, OCH=C*H*), 7.37 (1H, dd, $J = 1.5$ Hz, OC*H*); *m/z* (CI) 270 ($[M+H]^+$, 100%), 253 ($[M+H]^+$, 52%); HRMS $C_{13}H_{17}O_5$ ($[M+H]^+$) requires 253.1076; found 253.1080; **18** ν_{max} (film) 2950 (w), 2890 (w), 1728 (w), 1495 (w), 1452 (w), 1263 (w), 1211 (m), 1164 (w), 1079 (m), 1058 (w), 1027 (w) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 1.87 (1H, dt, $J = 3.0$, 13.5 Hz, PhC*H*), 2.25–2.35 (1H, m, OCH_2–C*H*H), 2.45–2.55 (1H, m, OCH_2–CH*H*), 2.55–2.65 (1H, m, CHPh–C*H*CH), 3.18 (1H, dd, $J = 3.5$, 13.5 Hz, PhCH–C*H*HPhC*H*), 4.09 (1H, dt, $J = 3.0$, 8.0 Hz, OC*H*H–CH_2), 4.28 (1H, q, $J = 8.0$ Hz, OC*H*H–CH_2), 4.75–4.82 (1H, m, OC*H*–CH=CH), 5.05 (1H, s, OC*H*O), 6.40 (1H, dd, $J = 6.0$, 16.0 Hz, OCH–C*H*=CH), 6.75 (1H, d, $J = 16.0$ Hz, OCH–CH=C*H*), 7.20–7.50 (10H, m, Ar); δ_C (50 MHz, $CDCl_3$) 31.9, 32.5, 44.5, 52.3, 53.7, 64.6, 72.3, 102.8, 127.0, 128.0, 128.2, 128.8, 129.0, 129.5, 131.6, 137.2, 140.5, 172.2; *m/z* (CI) 382 ($[M+NH_4]^+$, 63%), 365 ($[M+H]^+$, 15%), 347 (30%), 219 (100%), HRMS $C_{23}H_{24}O_4$ requires 364.1675; found 364.1673; **20** ν_{max} (film) 2949 (w), 1732 (s), 1495 (w), 1451 (w), 1202 (w), 1042 (s) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.00–2.12 (1H, m, PhCH–C*H*H), 2.30–2.40 (2H, m, PhCH–CH*H*, OCH_2–C*H*H), 2.60–2.70 (1H, m, OCH_2–C*H*H), 3.40 (3H, s, CO_2*Me*), 3.41–3.47 (1H, m, PhC*H*), 3.93 (1H, q, $J = 6.0$ Hz, OC*H*H–CH_2), 4.28 (1H, dt, $J = 2.5$, 9.0 Hz, OCH*H*–CH_2), 4.75 (1H, q, $J = 4.0$ Hz, OC*H*–CH=CH), 5.70 (1H, s, OC*H*O), 6.25 (1H, dd, $J = 6.0$, 16.0 Hz, OCH–C*H*=CH), 6.68 (1H, d, $J = 16.0$ Hz, OCH–CH=C*H*), 7.10–7.40 (10H, m, Ar); δ_C (50 MHz, $CDCl_3$) 32.3, 33.7, 44.7, 52.3, 59.2, 67.6, 71.3, 102.8, 126.9, 127.6, 128.1, 128.7, 128.1, 129.0, 129.8, 130.9, 137.1, 141.5, 173.3, *m/z* (CI) 383 ($[M+NH_4]^+$, 40%), 365 ($[M+H]^+$, 10%), 347 (30%), 219 (100%); HRMS $C_{23}H_{24}O_4$ requires 364.1475; found 364.1670; **24** ν_{max} (film) 2952 (s), 2930 (s), 2895 (m), 2857 (m), 1471 (w), 1463 (w), 1254 (m), 1147 (w), 1093 (s), 1076 (s), 1034 (m) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 0.00 (6H, s, SiMe_2), 0.85 (9H, s, Si-*t-Bu*), 1.40–1.70 (4H, m, H-4a, H-6a,b, H-7a), 1.80–2.00 (2H, m, H-4b, H-7b), 3.26 (1H, d, $J = 9.5$ Hz, SiOC*H*H), 3.30–3.40 (1H, m, H-8a), 3.42 (1H, d, $J = 9.5$ Hz, SiOCH*H*), 3.76–3.84 (1H, m, H-8b), 4.05 (1H, dt, $J = 4.5$, 8.5 Hz, H-3a), 3.90 (1H, q, $J = 8.5$ Hz, H-3b), 4.80 (1H, s, OC*H*O); δ_C (75 MHz, $CDCl_3$) −5.7, −5.6, 18.2, 21.1, 25.8, 26.2, 28.9, 46.5, 63.7, 66.5, 66.7, 102.3; *m/z* (CI) 290 ($[M+NH_4]^+$, 50%), 273 ($[M+H]^+$, 100%), 215 (18%); HRMS $C_{14}H_{29}O_3{}^{29}Si$ requires 273.1886; found 273.1887.

14. This ring system is present in a number of natural products. For leading references see: Messer, R.; Schmitz, A.; Moesch, L.; Häner, R. *J. Org. Chem.* **2004**, *69*, 8558–8560; Willis, M. C.; Flower, S. *Synlett* **2003**, 1491–1493; Brüggemann, M.; McDonald, A. I.; Overman, L. E.; Rosen, M. D.; Schwink, L.; Scott, J. P. *J. Am. Chem. Soc.* **2003**, *125*, 15284–15285.
15. cf. The following redox potentials:

$$Ce(IV) + e^- \leftrightarrow Ce(III)\ E^0 + 1.72\ V$$
$$[(Cp)_2Fe]^+ + e^- \leftrightarrow [(Cp)_2Fe]\ E^0 + 0.40\ V$$

(Housecroft, C. E.; Sharpe, A. G. In *Inorganic Chemistry*; Pearson: Harlow, 2001; pp 613, 629).
16. Competing intramolecuar Friedel–Crafts alkylation (see Fillion, E.; Beingessner, R. L. J. Org. Chem. **2003**, *68*, 9485–9488; Nagata, T.; Nakagawa, M.; Nishida, A. *J. Am. Chem. Soc*. **2003**, *125*, 7484–7485) was not observed.
17. The electrochemical oxidation of α-alkoxygermanes has been reported: Yoshida, J.; Morita, Y.; Itoh, M.; Ishichi, Y.; Isoe, S. *Synlett* **1992**, 843–844.
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19. Hydride transfer from stannylcarbinols has been employed in the synthesis of acylstannanes: Marshall, J. A.; Gung, W. Y. *Tetrahedron Lett.* **1989**, *30*, 2183–2186; Quintard, J.-P.; Elissondo, B.; Mouko-Mpegna *J. Organomet. Chem.* **1983**, *251*, 175–187; For examples of 1,5-hydride shifts see: Wöfling, J.; Frank, E.; Schneider, G.; Tietze, L. F. *Eur. J. Org. Chem.* **2004**, 90–100; Krohn, K.; Flörke, U.; Höfker, U.; Träubel, M. *Eur. J. Org. Chem.* **1999**, 3495–3499; An excellent review on this general area can be found in: Watt, C. I. F. *Adv. Phys. Org. Chem.* **1988**, *24*, 57–112.