

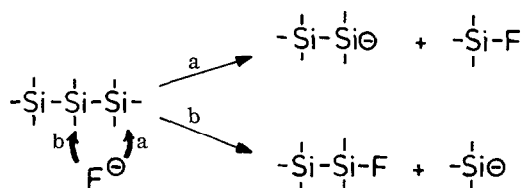
INSERTION OF ALKANAL CARBONYL AND 1,3-DIENE UNITS BETWEEN Si-Si BONDS  
 OF TRISILANES. SYNTHESIS OF NOVEL SILICON-CONTAINING MATERIALS

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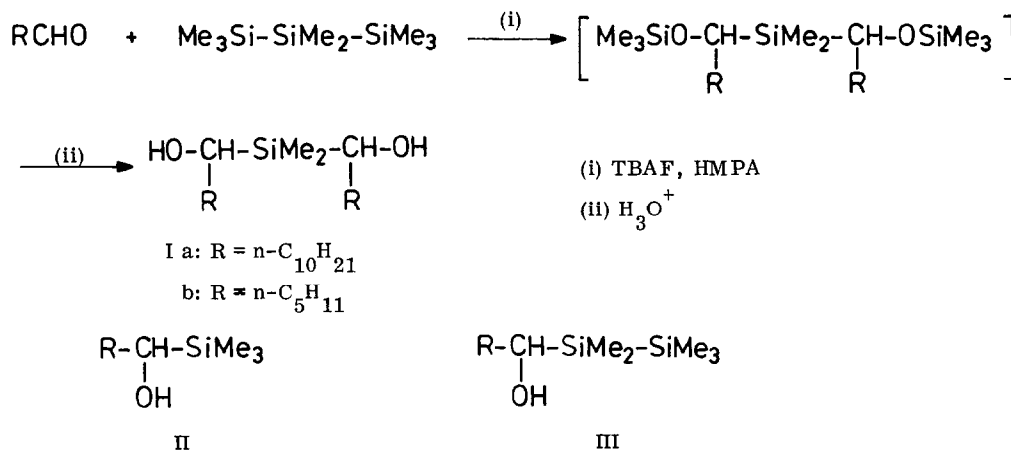
Octamethyltrisilane/tetrabutylammonium fluoride reagent allows us to insert A=B (e.g. alkanals and 1,3-dienes) between the Si-Si bonds to produce Si-A-B-Si-B-A-Si structure in one step or Si-A-B-Si-B'-A'-Si step by step.

Disilane/tetrabutylammonium fluoride (TBAF) reagent generates metal-free triorganosilyl anions and disilylates alkanals and 1,3-dienes.<sup>1</sup> This disilylation represents a new transformation which involves an insertion of alkanal carbonyl (RCH=O) or conjugated diene (CH<sub>2</sub>=CHCH=CH<sub>2</sub>) system into disilane Si-Si bond to afford Si-CHR-O-Si or Si-CH<sub>2</sub>CH=CHCH<sub>2</sub>-Si. Extension of this concept to trisilanes provokes new problems: possibility of double insertion (one step or stepwise) and regioselectivity of the fluoride attack. Attack of F<sup>-</sup> at the terminal silicon (route a) of trisilane should give disilyl anion, whereas attacking at the central silicon atom (route b) will provide silyl anion and disilyl fluoride. Experimental answers to these problems are reported herein.



Undecanal (0.155 ml, 0.75 mmol) was allowed to react with octamethyltrisilane<sup>2</sup> (0.197 ml, 0.75 mmol) in the presence of TBAF (0.5 M tetrahydrofuran solution, 0.1 ml, 0.05 mmol) in hexamethylphosphoric triamide (HMPA) (2 ml) overnight at room temperature under an argon atmosphere. Workup was effected by treating the reaction mixture with a 1:10 mixture (1 ml) of conc-hydrochloric acid and methanol and by extracting the resulting solution with ether. The ethereal extract was washed with brine, dried over magnesium sulfate and concentrated in vacuo. A crude product (181 mg) formed as an oil was purified by preparative TLC (hexane-ethyl acetate 5:1) to give Ia (95 mg, 63% yield)<sup>3, 4a</sup> as ca 1:1 diastereomeric mixture as revealed by <sup>1</sup>H NMR assay (GLC: single peak). Worthy to point out is that any trace of a trimethylsilyl adduct II<sup>1</sup> was not produced and that only a trace of disilyl adduct III was detected by GLC assay. Starting with hexanal, we obtained Ib<sup>3, 4b</sup> in 68% yield.

Exclusive formation of I clearly demonstrates that the path a in the scheme is markedly preferred. The highly selective fluoride attack may be attributed to the fact that silicon (1.74) is less electro-negative than carbon (2.50). Consequently, terminal silicon atoms are more electrophilic than the central one. It should be noted that trisilane/TBAF reagent may be used for a source of a disilyl anion.<sup>5</sup> Benzaldehyde was converted into 1,2-diphenylethane-1,2-diol like the disilane/TBAF catalyzed reaction<sup>1</sup> albeit in a lower yield (29%).



Insertion of 2-buten-1,4-diyl unit between the Si-Si bonds of trisilane was achieved by the reaction of octamethyltrisilane with 1,3-dienes. Thus, addition of TBAF catalyst (7 mol%) to an HMPA solution of octamethyltrisilane and butadiene (1:2 mol ratio), or addition of butadiene to an HMPA solution of octamethyltrisilane and TBAF catalyst gave Va<sup>3,4c</sup> in 30-34% isolated yields along with a higher homolog whose structure is assigned as VIa<sup>3,4d</sup> (ca 10% yields). The olefin geometry of products is assumed to be (E) on the basis of IR spectra (960 cm<sup>-1</sup>) as well as our previous observations.<sup>1</sup> Formation of VIa may be ascribed to the fluoride anion attack at the internal disilane silicon atom of the initially formed IVa to produce Si-CH<sub>2</sub>CH=CHCH<sub>2</sub>-Si-F which is trapped by SiCH<sub>2</sub>CH=CHCH<sub>2</sub>-Si-CH<sub>2</sub>CH=CHCH<sub>2</sub><sup>-</sup> generated by fluoride attack at the terminal disilane silicon atom of IVa followed by the reaction with butadiene.<sup>6</sup> A different product was produced by adding octamethyltrisilane to an HMPA solution of butadiene and TBAF catalyst, hereby giving rise to a disilane IVa (23% yield)<sup>3,4e</sup> and Va (8% yield) without formation of VIa.

The reaction of octamethyltrisilane with 2,3-dimethylbutadiene proceeds stepwise. Irrespective of the addition order, disilane IVb<sup>3,4f</sup> was produced in 68-69% yields. The disilane IVb thus formed is found to be converted to Vb<sup>3,4g</sup> by additional TBAF catalyst (7 mol%) in 43% overall yield along with a trace of IVb.<sup>4h</sup>



4. (a) Mp 45-46.5°C; IR (KBr) 3350, 1470, 1380, 1250, 940, 840, 780  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CCl}_4$ )  $\delta$  -0.10-0.02 (4s, 6 H), 0.84 (t,  $J = 6$  Hz, 6 H), 1.00-1.70 (m, 36 H), 3.25-3.45 (m, 2 H), 3.45-3.67 (m, 2 H).
- (b)  $R_f$  0.20 (hexane-ethyl acetate 5:1); IR (neat) 3350, 1470, 1380, 1250, 940, 842, 781  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CCl}_4$ )  $\delta$  -0.10-0.20 (4s, 6 H), 0.85 (t,  $J = 6$  Hz, 6 H), 1.00-1.65 (m, 16 H), 2.70-2.90 (m, 2 H), 3.20-3.50 (m, 2 H).
- (c) Bp (Kugelrohr) 125-140°C/2 Torr; IR (neat) 1250, 1158, 1054, 960, 840, 690  $\text{cm}^{-1}$ ; MS m/z (rel %) 312 ( $\text{M}^+$ , 1), 185 (6), 97 (18), 73 (100), 45 (6);  $^1\text{H NMR}$  ( $\text{CCl}_4$ )  $\delta$  -0.05 (s, 24 H), 1.20-1.40 (m, 8 H), 5.00-5.20 (m, 4 H).
- (d) Bp (Kugelrohr) 190-200°C/2 Torr; IR (neat) 1250, 1158, 1053, 960, 840, 690  $\text{cm}^{-1}$ ; MS m/z (rel %) 424 ( $\text{M}^+$ , 1), 297 (2), 185 (7), 169 (3), 97 (20), 73 (100), 59 (4);  $^1\text{H NMR}$  ( $\text{CCl}_4$ )  $\delta$  -0.03 (s, 30 H), 1.25-1.45 (m, 12 H), 5.00-5.23 (m, 6 H).
- (e) Bp (Kugelrohr) 130-140°C/17 Torr; IR (neat) 1245, 1155, 1052, 960, 830, 720, 690, 610  $\text{cm}^{-1}$ ; MS m/z (rel %) 258 ( $\text{M}^+$ , 4), 155 (6), 132 (10), 131 (76), 97 (10), 73 (100), 45 (12);  $^1\text{H NMR}$  ( $\text{CCl}_4$ )  $\delta$  0.00-0.20 (m, 24 H), 1.33-1.60 (m, 4 H), 5.10-5.27 (m, 2 H).
- (f) Bp(Kugelrohr) 150-170°C/20 Torr; IR (neat) 1250, 1172, 1050, 835, 810, 690  $\text{cm}^{-1}$ ; MS m/z (rel %) 286 ( $\text{M}^+$ , 11), 132 (12), 131 (75), 125 (28), 73 (100), 45 (10);  $^1\text{H NMR}$  ( $\text{CCl}_4$ )  $\delta$  -0.03-0.15 (m, 24 H), 1.40-1.60 (m, 10 H).
- (g) Bp (Kugelrohr) 160-180°C/3 Torr; IR (neat) 1370, 1250, 1170, 900, 838, 760  $\text{cm}^{-1}$ ; MS m/z (rel %) 368 ( $\text{M}^+$ , 3), 213 (2), 139 (18), 125 (51), 73 (100), 59 (11);  $^1\text{H NMR}$  ( $\text{CCl}_4$ )  $\delta$  -0.03 (s, 9 H), 1.37-1.55 (m, 20 H).
- (h) IR (neat) 1375, 1250, 1172, 905, 840, 690  $\text{cm}^{-1}$ ; MS m/z (rel %) 508 ( $\text{M}^+$ , 2), 213 (6), 197 (7), 139 (25), 125 (76), 73 (100), 59 (10), 45 (4);  $^1\text{H NMR}$  ( $\text{CCl}_4$ )  $\delta$  0.10 (s, 30 H), 1.50-1.70 (m, 30 H).
- (i)  $R_f$  0.60 (hexane-ethyl acetate 5:1); IR (neat) 3450, 1372, 1250, 1170, 905, 840, 760, 690  $\text{cm}^{-1}$ ; MS m/z (rel %) 314 ( $\text{M}^+$ , 2), 155 (11), 133 (4), 125 (5), 75 (53), 73 (100), 59 (6), 45 (5);  $^1\text{H NMR}$  ( $\text{CCl}_4$ )  $\delta$  0.07 (s, 15 H), 0.93 (t,  $J = 6$  Hz, 3 H), 1.10-1.65 (m, 18 H), 3.27 (t,  $J = 6$  Hz, 1 H).
5. Pentaphenyldisilyllithium: Steward, O. W.; Heider, G. L.; Johnson, J. S. *J. Organomet. Chem.* **1979**, 168, 33; Wittenberg, D.; George, M. V.; Gilman, H. *J. Am. Chem. Soc.* **1959**, 81, 4812. Tris(trimethylsilyl)silyllithium: Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, 225, 1.
6. Another possible explanation is the disproportionation of trisilane upon the reaction with TBAF catalyst. In fact, in the absence of butadiene octamethyltrisilane was converted into higher polysilanes.

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