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SILICON IN SYNTHESIS—17

CHLOROMETHYL(TRIMETHYLSILYL)LITHIUM—A NEW REAGENT FOR THE DIRECT CONVERSION OF ALDEHYDES AND KETONES INTO α,β-EPOXYTRIMETHYLSILANES

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Abstract—Treatment of chloromethyltrimethylsilane **1** with sec-BuLi in THF at −78° produces chloromethyl(trimethylsilyl)lithium **4**. Treatment of **4** with a wide range of aldehydes and ketones gives α,β-epoxytrimethylsilanes **5–28**, which on acidic hydrolysis give homologated aldehydes.

In 1946, Sommer and Whitmore[1] described for the first time, the preparation of trimethylsilylmethylmagnesium chloride **2** from chloromethyltrimethylsilane **1**, and Mg metal. It was not until 1968 that Peterson demonstrated the valuable synthetic uses of this Grignard reagent for the preparation of terminal alkenes.[2] Since the latter date many extensions and applications of the so-called Peterson reaction have been described, in particular during the last several years.[3] It is also interesting to note that Sommer also described in detail the preparation of trimethylsilylmethyllithium **2**, a reagent that quickly found very useful applications in organometallic chemistry.[4] Trimethylsilylmethyllithium **2** is prepared from **1** and Li metal in olefin-free pentane. After decanting the insoluble lithium chloride, the solutions of **2** are very stable. Indeed cooling 1.0 M pentane solutions of **2** below approximately −10° produces large crystals of **2** that can be sublimed as a method of purification for organometallic work.[5]

$$\underset{\underline{1}}{Me_3SiCH_2Cl} \xrightarrow{Mg \text{ or } Li} \underset{\underline{2}}{Me_3SiCH_2MgCl \text{ or } Li}$$

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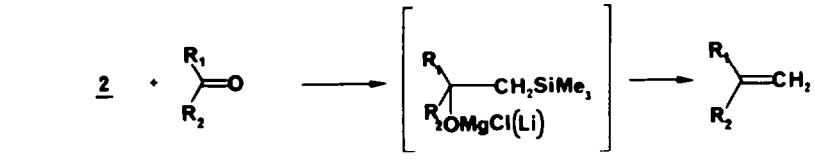
It is particularly pertinent that prior to the work described here, all variations of the Peterson reaction, where the elimination of trimethylsilanate is competitive with other facile elimination processes (Scheme A), the elimination of trimethylsilanate was the only observed reaction.[6]

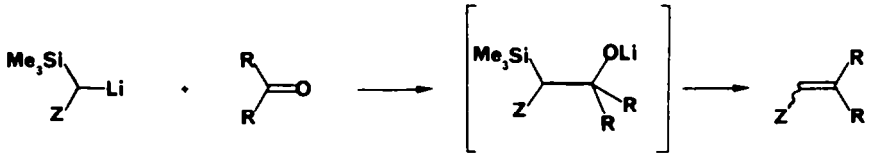
α,β-Epoxyalkylsilanes **3** were introduced as a useful functional group in organic synthesis by Stork and Colvin.[7] They showed that epoxidation of a vinylsilane gave an epoxyalkylsilane **3**, which on acid hydrolysis gave an aldehyde or ketone. This type of transformation provided a valuable solution to a particular variation on alkylative annulation reactions. (Scheme B).[8] The mechanistic details of how α,β-epoxyalkylsilanes are transformed into aldehydes, and their general interaction with electrophiles has been elucidated by Hudrlik.[9]

Most importantly, from the standpoint of the work described here, α,β-epoxyalkylsilanes were only available by epoxidation of vinylsilanes; and since vinylsilanes are, in the most general sense, only accessible by either the hydrosilylation of acetylenes, or hydrogenation of alkylsilylacetylenes, none of these methods involve the formation of a new C–C bond.[10]

The basic premise of the research described in this paper is the preparation of α,β-epoxyalkylsilanes by a C–C *bond forming reaction.* As such, as will be seen, this chemistry has its closest analogy in the classical Darzens reaction.

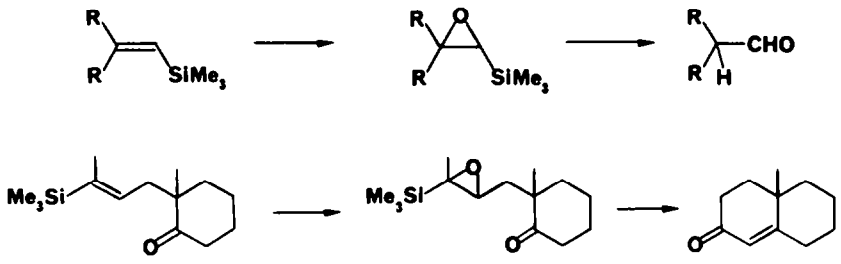


PETERSON OLEFINATION REACTION



Z = P(O)(OEt)$_2$; PPh$_2$ etc.[3]

Scheme A.



Scheme B.

RESULTS

While we were engaged in research directed toward the synthesis of highly oxygenated sesquiterpenes[11] an occasion arose to convert an aldehyde into a vinyl group. We elected to use the Peterson reaction to conduct this transformation. During this research, combined with the awareness, as alluded to above, that α,β-epoxyalkylsilanes were only available through reactions that did not involve C–C bond formation, we decided to examine the possibility of deprotonating chloromethyltrimethylsilane **1** to give chloromethyl (trimethylsilyl)lithium **4**. This is a perfectly reasonable thing to attempt, especially since Köbrick[12] and Seyferth[13] had shown that α-halomethyllithium species are readily prepared. Although for the case of **1** the choice of the base can be predicted to be crucial, since nucleophilic attack at silicon might be a competing reaction pathway.[14] Perhaps more interestingly, given that the appropriate base can be found, and solutions of **4** made; it would be predicted on the basis of a substantial volume of prior literature[3] that adducts with aldehydes or ketones **4a** (see Scheme A) would eliminate trimethylsilanate to give vinylchlorides rather than α,β-epoxyalkylsilanes (Scheme C). Given this rather dismal prognosis one might well, and with ample literature justification, not pursue this proposal further.[15]

Treatment of chloromethyltrimethylsilane **1** with sec-BuLi (1.05 M in cyclohexane or n-hexane) in THF at −78°, in the presence of TMEDA (1.05 equiv) gave solutions of **4** in ≥95% yield (as judged by subsequent treatment with carbonyl electrophiles). The presence of TMEDA is not essential but generally improves the rate of formation of **4**. We examined several other bases and the results are summarized in the Table 1.

Without doubt sec-BuLi is by far the most efficient base; this can be largely attributed to steric factors, assuming the reactive species in THF solution is monomeric sec-BuLi in equilibrium with aggregated species. n-BuLi is small enough to attack the Si-atom giving an "ate" complex that can migrate alkyl groups with the loss of Cl^-. t-BuLi is too large and prefers the bulky Cl-atom, resulting in Cl-Li exchange. (Fig. 1).

Solutions of **4** were treated with aldehydes and ketones, generally between −78° and 20°, to give, without exception α,β-epoxysilanes Table 2. We were unable to detect vinylchlorides (VPC and NMR within 5%).

Under these conditions **4** does not α-eliminate to give the carbenoid species, **4b**, although Olofson, Chapman,

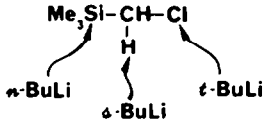
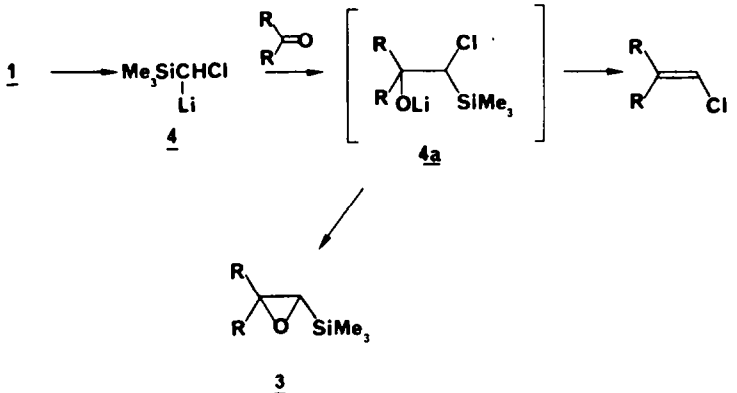


Fig. 1.

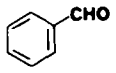
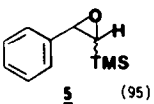
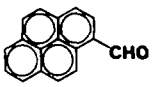
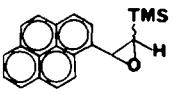
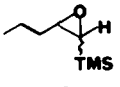
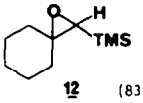
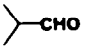
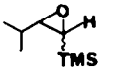
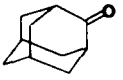
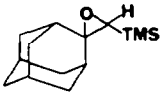
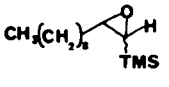
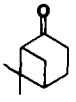
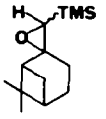
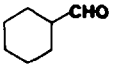
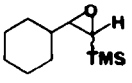
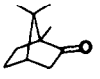
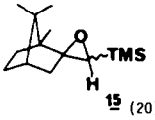
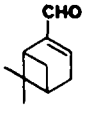
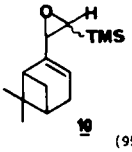
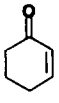
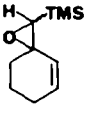
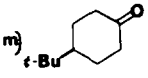
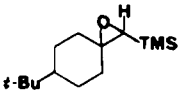
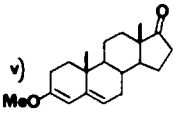
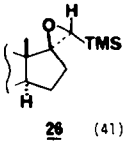
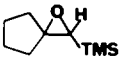
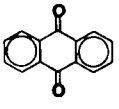
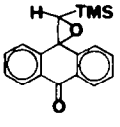
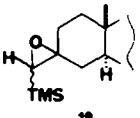
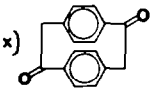
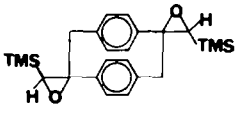
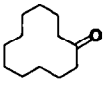
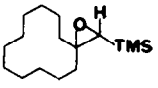
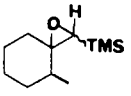
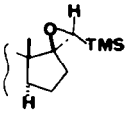
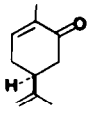
Table 1.

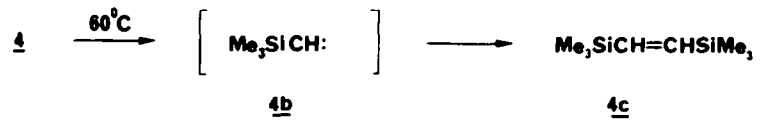
Base/°C	% of 4	
$LiNPr^i_2$/ − 78°C	8%	
$LiNPr^iC_6H_{11}$/ − 78°C	≥8%	These figures were determined by vpc analysis of the reaction of **4** with cyclohexanone to give the α,β-epoxysilane **12**.
$LiN(SiMe_3)_2$/ − 78°C	40%	
n-BuLi/-78°C/TMEDA	25%	
t-BuLi/-78°C/TMEDA	≤8%	



Scheme C.

Table 2.

SUBSTRATE	EPOXYTRIMETHYLSILANE (%)	SUBSTRATE	EPOXYTRIMETHYLSILANE (%)
a) 	 **5** (95)	g) 	 **11** (81)
b) 	 **6** (40)	h) 	 **12** (83)
c) 	 **7** (70)	i) 	 **13** (95)
d) $CH_3(CH_2)_6CHO$	$CH_3(CH_2)_6$  **8** (82)	j) 	 **14** (24)
e) 	 **9** (94)	k) 	 **15** (20)
f) 	 **10** (95)	l) 	 **16** (52)
m) 	 **17** (88)	v) 	 **26** (41)
n) 	 **18** (85)	w) 	 **27** (89)
o) Cholestan-3-one	 **19** (90)	x) 	 **28** (89)
p) 	 **20** (57)	r) 	 **22** (77)
q) Estrone-O-methyl ether	 **21** (36)	t) 	**24** (76)
s)	**23** (76)	u)	**25** (58)



Shechter and Chedekel[16] have examined the carbenoid chemistry of **4b**. If solutions of **4** are heated to 60° then decomposition does take place to give 1,2-bistrimethylsilylethylene **4c**.

The entry a), Table 2, is the only example where the intermediate chlorohydrin has been detected and isolated. Conducting the reaction of **4** with benzaldehyde at −55° gave the *threo*-chlorohydrin **5a**, along with the *E*-epoxide **5**. Treatment of *threo* **5a** with NaH/THF at 60° gave the *Z*-epoxide **5** thus confirming the stereochemical assignment for **5a**. While *threo* **5a** could be isolated, the *erythro*-isomer had closed to give the *E*-epoxide **5** even at −55°. The slower closure of the *threo*-isomer **5a** is to be expected, since it involves eclipsing the two large substituents in the transition state.

In general for all of the entries a)–x), the starting aldehyde or ketone was consumed by CTC **4** (chloromethyl(trimethylsilyl)carbanion)[17] at −78° to give polar product(s) (TLC), presumably, by analogy with **5**, chlorohydrins. On warming the reaction mixture from −78° to between −30° and −40° the polar material rapidly disappeared and was replaced by the desired less polar α,β-epoxytrimethylsilanes **5–28**.

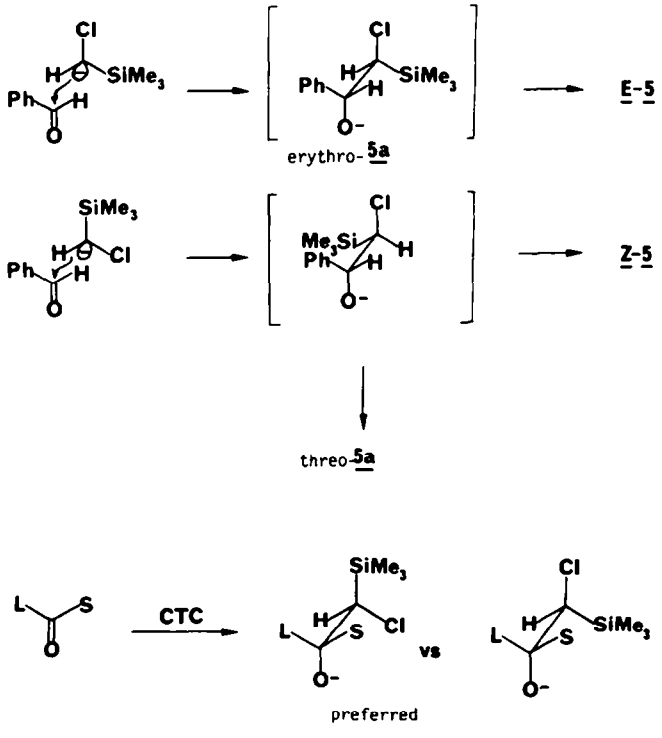
Sterically unhindered aldehydes and ketones, entries a)–l), l)–p), r)–u), w) and x) pose no problems. The α,β-epoxytrimethysilane adducts are formed in good to excellent yields. Sterically hindered ketones, especially nopinone and camphor, j) and k) gave low yields of α,β-epoxytrimethylsilane adducts. In particular the 17-ketosteroids, q) and v) gave at best only moderate yields. Increasing the number of equivalents of **4** did not alleviate the situation. Attempts to increase the nucleophilicity of CTC by converting it to the ZnCl salt, or the addition of $LiClO_4$, rather than improve yields, drastically decreased them.

In most cases where the diastereotopic faces of the carbonyl compound are very different the CTC approaches from the sterically less crowded face, k), q), s), v). Where the α,β-epoxytrimethylsilanes can be formed as epimers at the carbon bearing the trimethylsilyl group, the predominant epimer is the one that results from having the trimethylsilyl group in the least sterically encumbered environment. (Scheme D). For most of the examples in Table 2 there is little difference, but for the reaction of CTC with dihydro-β-ionone to give **42** there is a marked preference.

Readily enolizable aldehydes and ketones such as **29–32** did not form α,β-epoxytrimethylsilanes in more than 5% yield on treatment with **4**. In the case of **32**, treatment with **4** caused clean conversion to the aldol product **33**. The diketone **34** did not show any selectivity towards CTC; both the CO groups formed α,β-epoxytrimethylsilane adducts.

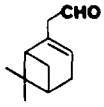
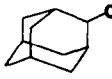
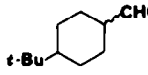
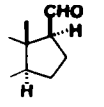
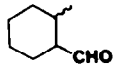
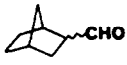
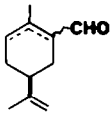
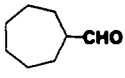
Transformations of α,β-epoxytrimethylsilanes

Mild acid hydrolysis (20% aqueous THF/5–10% $HClO_4$) of the α,β-epoxytrimethylsilanes usually resulted in clean conversion into the homologous aldehydes[7] Table 3. In the cases **11**, **27** and **28**, complex mixtures of products were formed with no detectable amounts of aldehydes present (NMR). Interestingly using the above acidic conditions, **23** gave, as expected the homologous aldehyde (entry j) Table 3). Whereas exposure of **23** to



Scheme D.

Table 3.

	EPOXYTRIMETHYLSILANE	ALDEHYDE (%)
a)	5	$PhCH_2CHO$ (85)
b)	8	$CH_3(CH_2)_6CHO$ (85)
c)	10	 (94)
d)	12	 (74)
e)	13	 (71)
f)	17	 (72)
g)	22	 (98)
h)	22	 (77)
i)	23	 (73)
j)	24	 (78)
k)	25	 (98)

90% formic acid resulted in rearrangement to the ketone **35**.[18]

Hydrolysis of **27** caused deformylation to give 9-anthrone.[19] Since α,β-epoxytrimethylsilanes has been shown to be readily converted into vinylbromides, enamides, and enol ethers,[20] we examined further some transformations of epoxysilanes that would increase their scope as a useful functional group in synthesis.

Treatment of **12** with ethylene glycol in benzene in the presence of a catalytic amount of *p*-toluenesulfonic acid, cleanly gave the acetal **36**. Similarly the thioanalogs shown below were readily prepared. When **12** was treated with hydrogen peroxide in acetic acid it was slowly converted into cyclohexane carboxylic acid (60%).

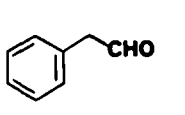
Eisch[21] has shown the α,β-epoxytrimethylsilanes can be deprotonated to give lithiospecies such as **37**. For the specific substrate **12** we found that *t*-BuLi in THF at −70° gave the lithioepoxysilane **37**, as judged by its subsequent conversion with electrophiles (Scheme D).

To demonstrate the effective use of the reagent **4** in organic synthesis the unusual enol formate *Latia Luciferin* **41**, the specific substrate in bioluminescence of the luciferase system in the fresh water limpet *Latia neritoides*, was chosen as a suitable target.[22]

Treatment of dihydro-β-ionone[23] with **4** gave **42** in 85% yield, as a single stereoisomer (as evidenced by NMR ≥ 95%). The assigned stereochemistry is based upon the subsequent conversion of **42** into *Latia Luciferin* **41**. The epoxytrimethylsilane **42** was treated with anhydrous formic acid to give *Latia Luciferin* **41**. The epoxytrimethylsilane **42** was treated with anhydrous formic acid to give *Latia Luciferin* **41** via the *anti*-elimination of trimethylsilanol. The final product **41** was assigned the *E*-configuration on the basis of the chemical shift of the olefinic proton (δ 7.97) for the *E*-isomer.

Approximately 10% of the *Z*-isomer of *Latia Luciferin* contaminated the natural *E*-isomer.[24] The overall yield of **41** is 80%, and an effective illustration of α,β-epoxytrimethylsilanes as precursors to enol derivatives.

Attempts to generalize the reagent **4** by alkylation were not successful. Alkyllithiums could not be added to 1-chloro-1-trimethylsilylethylene **43**, to form new derivatives of **4**.[25] We could not prepare cuprates of **4** without reductive coupling.



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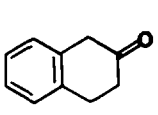

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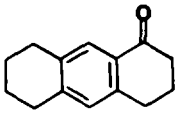

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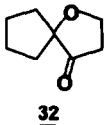

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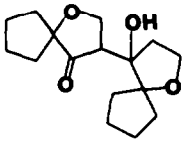

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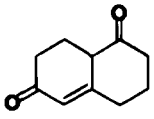

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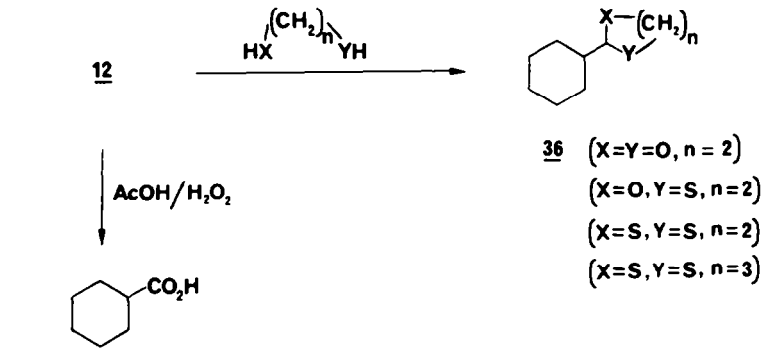
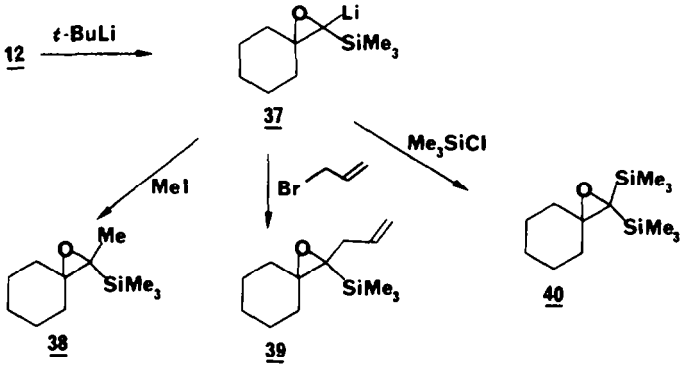
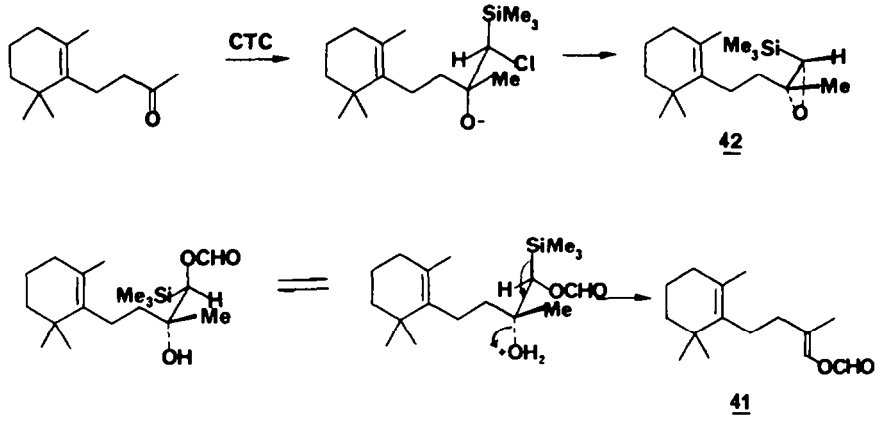
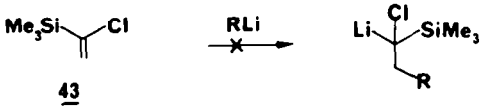




Scheme D.



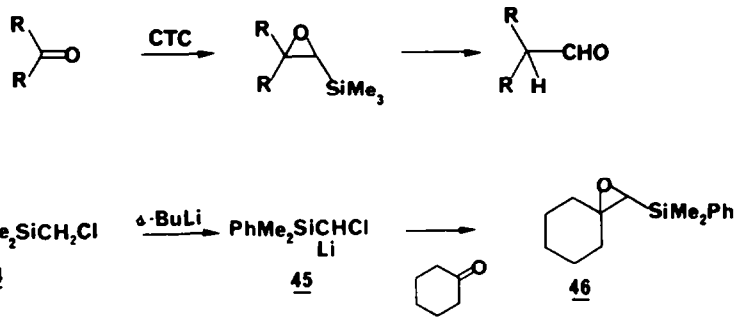


In summary, the reagent chloromethyl(trimethylsilyl)lithium **4** provides a direct way of converting aldehydes or ketones into α,β-epoxytrimethylsilanes. Mild acid hydrolysis of these adducts gives aldehydes, thus providing a new method of homologating CO groups. This particular type of reaction may be called *reductive nucleophilic acylation*, because **4** is an acyl anion equivalent, and the original CO carbon atom is reduced in the final homologated aldehyde.[39]

Finally it should be noted that chloromethyl(dimethylphenyl)silane **44** was readily deprotonated on treatment with s-BuLi to give the Li derivative **45**. Quenching **45** with cyclohexanone gave the desired epoxysilane **46**, unfortunately acid hydrolysis of **46** gave a complex mixture with little of the expected cyclohexanecarboxyaldehyde present. Apparently Si–Ph electrophilic cleavage takes place more readily than opening of the epoxide, and as a result complex mixtures were formed.[26]

EXPERIMENTAL

Gas chromatographic analyses were performed with a Perkin–Elmer 3920B instrument using 10% OV101 on chrom WHP (80–100) or 10% SE-30 on chrom DAW(100–200). Preparative layer chromatography was carried out eluting with petroleum ether (b.p. 60°–90°)/EtOAc (4:1) unless otherwise specified. IR spectra were recorded on a Perkin–Elmer 267 Grating spec-



trometer, and are for neat liquids unless otherwise specified. ^{1}H NMR spectra were recorded on a Varian A-60, Varian EM-360, or Varian EM-390 spectrometer for solns in CCl_4, with TMS (2%) as internal standard, unless stated otherwise. Mass spectral data were obtained using a Double Focussing Consolidated Electronic MS-9 mass spectrometer. All bps are uncorrected. Mps were taken on a Thomas Hoover mp apparatus and are uncorrected. Solvents were dried and purified by standard techniques prior to use. Experiments involving alkyllithiums or amide bases were conducted under argon or N_2. Transfer of liquids was carried out under a positive pressure of argon or N_2 using syringes oven dried to 160°.

s-BuLi (1.1 M or 1.3 M, in cyclohexane) was purchased from Foote Mineral Company, and found to be the most reliable source of this material. Chloromethyltrimethylsilane was purchased from Petrarch Systems Inc., distilled (b.p. 97°/760 mm) before use and stored over molecular sieves (4 Å).

General procedure for the preparation of THF/cyclohexane solutions of chloromethyl(trimethylsilyl)lithium **4**. sec-BuLi (1.1 M in cyclohexane, 1.05 equivs) was added dropwise to a magnetically stirred soln of chloromethyltrimethylsilane **1** (1.0 equivs) in dry THF (to give an approximately 1 M soln of **4**) at −78° under argon. A yellow soln was formed. After 5 min TMEDA (1.05 equivs) was added and the soln stirred for 0.5 hr allowing the temp to rise to −55°, when the color became very pale yellow. The above soln of CTC (chloromethyltrimethylsilyl carbanion) may be used at −55°; or at temps ranging from −78° to 25°. It is advisable to use the freshly prepared reagent for best results.

(E, Z)-3-*Phenyl*-2-*trimethylsilyloxirane* **5**. Benzaldehyde (0.53 g 4.93 mmol) was added slowly to a soln of CTC (6.15 mmol) in THF (8 ml) at −55°. The soln was maintained at −50° for 0.5 hr then warmed to 20° over 3 hr. The mixture was poured into 0.5 M HCl (25 ml), extracted with CH_2Cl_2 (3 × 30 ml), dried ($MgSO_4$) and evaporated to give **5** as an oil (0.87 g 95%–98% pure 3.4:1/Z:E glc), IR 1605, 1595, 1248, 842, 750 cm^{-1}. NMR δ 7.47(5H, s), 4.40(1H, d J = 5 Hz), 3.86(1H, d J = 3 Hz), 2.68(1H, d J = 5 Hz), 2.48(1H, d J = 3 Hz), 0.31(9H, s), 0.19(9H, s). MS (on isomeric mixture) $C_{11}H_{16}OSi$ requires: 192.097, OBs: 192.097.

Conducting the above experiment, but keeping the temp at −55° gave after work-up, and crystallization from petroleum ether (b.p. 40–50°) 1-*phenyl*-2-*chloro*-2-*trimethylsilyl ethanol* **5a**. (19%), m.p. 64–65°. IR (Nujol mull) 3400, 1248, 1060, 870, 840, 745, 695 cm^{-1}. NMR δ 7.46(5H, s), 4.84(1H, d J = 6 Hz), 3.62(1H, d J = 6 Hz), 2.80(1H, s), 0.07(9H, s). (Found: C, 57.74; H, 7.35: $C_{11}H_{17}ClOSi$ requires: C, 57.89; H, 7.45%).

Treatment of **5a** (0.03 g) in THF (1 ml) with NaH (0.06 g) at reflux for 6 hr gave exclusively *Z*-**5**(0.02 g). NMR δ 7.48(5H, s), 4.47(1H, d J = 5 Hz), 2.63(1H, d J = 5 Hz), 0.19(9H, s). (E,Z)-3-*Propyl*-2-*trimethylsilyloxirane* **6**. Butyraldehyde (0.14 g 2.0 mmol) was treated with CTC (2.4 mmol) in THF (4 ml) at −55°, then warmed to 20° over 2 hr. Work-up as for **5** gave **6** (0.27 g). Distillation b.p. 45–48°/2 mm gave pure (98% glc) **6** (0.12 g 40%). NMR δ 2.21(1H, *b*), 1.5–0.9(8H, m), 0.11(9H, s). $MSC_8H_{18}OSi$ requires: 158.112, OBs: 158.113.

(E,Z)-3-*Isopropyl*-2-*trimethylsilyloxirane* **7**. Isobutyraldehyde (1.26 ml 0.0138 mol) was treated with CTC (1.2 equiv) at −78° for 15 min then warmed to 20°. Workup with sat NH_4Claq, followed by extracting with ether gave **7** (1.5 g 70%), b.p. 24–25/0.125 mm. NMR δ 2.40–2.60(1H, m), 2.0(1H, d J = 5 Hz), 0.85–1.15(7H, m). 0.1 and 0.0(9H, two singlets 1:1 for *E*, *Z*-isomers). MS $C_8H_{18}OSi$ requires: 158.112, Obs: 158.113.

(E,Z)-3-*Nonyl*-2-*trimethylsilyloxirane* **8**. η-Decanal (2.6 ml 0.0138 mol) was treated with TCT (1.2 equiv) at −78° for 15 min then warmed to 20°. Work-up as for **7** gave after distillation **8** (2.8 g 82%), b.p. 76–78°/0.10 mm. NMR δ 2.20(1H, b), 1.50–1.20(16H, bm), 0.85(3H, bs), 0.10(9H, s); and b.p. 82–84°/0.10 mm, similar NMR except 0.15(9H, s) attributable to *E*/*Z*-isomers 3:1. IR 2950, 1460, 1250, 845 cm^{-1}. (Found: C, 69.21; H, 12.06: $C_{14}H_{30}OSi$ requires: C, 69.42; H, 12.39%).

3-*Cyclohexyl*-2-*trimethylsilyloxirane* **9**. Cyclohexanecarboxaldehyde (0.19 ml 1.59 mmol) was treated with CTC (1.2 equiv) at −78° for 15 min then warmed to 20°. Work-up as for **7** gave **9** (0.296 g 98% pure by glc 94%) NMR δ 2.1(1H, d J = 5 Hz), 0.9–1.8(12H, bm), 0.01 and 0.0(9H, two singlets 1:1 for *E*,*Z*-isomers). IR 2920, 1450, 1250, 890, 870 cm^{-1}. MS $C_{11}H_{22}OSi$ requires: 198.144, OBs: 198.144.

3-[2-(6,6*Dimethylbicyclo*[3.1.1]*hept*-2-*ene*)]-2-*trimethylsilyloxirane* **10**. Myrtenal (1.0 g 6.65 mmol) was treated with CTC (1.5 equiv) at −78° for 15 min then 0° for 1.5 hr. Work-up as for **7** gave **10** (1.5 g 95%) b.p. 73°/0.3 mm. NMR δ 5.4(1H, bs), 3.1(1H, bs), 2.0–2.4(5H, bm), 1.3(3H, s), 1.0–1.2(2H, m), 0.9(3H, m), 0.1 and 0.15(9H, two singlets 2:1 for *E*,*Z*-isomers). IR 2920, 1250, 840 cm^{-1}. MS $C_{14}H_{24}OSi$ requires: 236.159, Obs: 236.157.

3-(1-*Pyrenyl*)-2-*trimethylsilyloxirane* **11**. 1-Pyrene carboxaldehyde (0.5 g 2.1 mmol) was treated with CTC (3 equiv) at −40°, then warmed to 20° over 1.5 hr. Work-up as for **5** gave a thick oil that was purified by preparative layer chromatography to give **11** (0.53 g 81%). IR 2920, 2860, 1250, 870 cm^{-1}. MS $C_{21}H_{20}OSi$ requires: 316.128, Obs: 316.127.

Cyclohexan - 1 - *oxiran* - 2 - *ylmethyltrimethylsilane* **12**. Cyclohexanone (0.58 g 5.70 mmol) was treated with CTC (6.2 mmol) at −50°. After 30 min work-up as for **5** gave **12** (0.88 g 83%), NMR δ 1.82(1H, s), 1.5(10H, s), 0.08(9H, s). IR 1248, 890, 840 cm^{-1}. (Found: C, 64.98; H, 11.03: $C_{10}H_{20}OSi$ requires: C, 65.16; H, 10.92%).

Adamantan - 2 - *oxiran* - 3 - *ylmethyltrimethylsilane* **13**. Adamantanone (0.30 g 2.0 mmol) was treated with CTC (4.0 mmol) at −60° for 0.5 hr then warmed to −30° for 0.5 hr. Work-up as for **5** gave **13** (0.47 g 95% ≥ 98% pure by glc). NMR δ 1.90–1.70(10H, m), 1.4–0.9(5H, m), 0.08(9H, s). IR 1420, 1248, 865, 840, 755 cm^{-1}. MS $C_{14}H_{24}OSi$ requires: 236.159, Obs: 236.160.

Nopinan - 1 - *oxiran* - 2 - *ylmethyltrimethylsilane* **14**. Nopinone (0.28 g 2.0 mmol) was treated with CTC (4.0 mmol) at −55° for 1 hr then warmed to 0° over 1 hr. Workup as for **5** gave a colorless oil (0.37 g) which was purified by preparative layer chromatography to give **14** (0.108 g 24%), NMR δ 2.7–1.6(9H, m), 1.30, 1.20, 0.90, 0.88(6H, two singlets 1:1 for epimers), 0.05, 0.01 (9H, two singlets 1:1 for epimers). (Found: C, 69.40; H, 10.67: $C_{13}H_{24}OSi$ requires: C, 69.64; H, 10.71%).

7,7,2 - *Trimethylbicyclo*[2.2.1]*heptan* - 1 - *oxiran* - 2 - *ylmethyltrimethylsilane* **15**. (+)-Camphor (0.30 g 2.0 mmol) was treated with CTC (6.0 mmol) at −55° for 0.5 hr. Work-up as for **5** gave a thick oil (0.25 g) which was purified by preparative layer chromatography to give **15** (0.094 g 20%), NMR δ 2.5–1.2(8H, m), 1.1–0.90 (9H, six singlets for epimers), 0.16, 0.04(9H, two singlets for epimers). (Found: C, 70.34; H, 10.97: $C_{14}H_{26}OSi$ requires: C, 70.59; H, 10.92%).

Cyclohex - 2 - *ene* - 1 - *oxiran* - 2 - *ylmethyltrimethylsilane* **16**.

2 - Cyclohexen - 1 - one (1.93 g 20.2 mmol) was treated with CTC (30 mmol) at −60° for 0.5 hr then warmed to 20° over 1 hr. Work-up as for **7** gave **16** (1.89 g 52%) b.p. 58°–62°/1.2 mm Hg (95% pure, glc). NMR δ 6.1–5.0(2H, m), 2.0–1.7(8H, b), 0.08–0.06(9H, two singlets for epimers). IR 3015, 1645, 1248, 1160, 900, 880, 755, 695 cm^{-1}. MS. $C_{10}H_{18}OSi$ requires: 182–113, OBs: 182.113.

4 - *t* - *Butylcyclohexan* - 1 - *oxiran* - 2 - *ylmethyltrimethylsilane* **17**. 4 - t - Butylcyclohexanone (0.308 g 2 mmol), was treated with CTC (2.4 mmol) at −55°, for 10 min. Work-up as for **7** gave **17** (0.425 g 88%, ⩾98% pure by glc). NMR δ 2.3–0.7(10H, m), 0.8(9H, s), 0.1(9H, s). MS. $C_{14}H_{28}OSi$ requires: 240.191, Obs: 240.191.

Cyclopentan - 1 - *oxiran* - 2 - *ylmethyltrimethylsilane* **18**. Cyclopentanone (0.18 ml 2.0 mmol) was treated with CTC (2.4 mmol) at −55° for 5 min. Work-up as for **7** gave **18** (0.290 g 85%). NMR δ 2.3–1.3(9H, m), 0.1(9H, s). IR 2950, 1400, 1250, 900, 840, 750 cm^{-1}. (Found: C, 63.24; H, 10.70: $C_9H_{18}OSi$ requires: C, 63.53; H, 10.59%).

Cholestan - 3 - *oxiran* - 2 - *ylmethyltrimethylsilane* **19**. Cholestan - 3 - one (0.387 g 1.0 mmol) was treated with CTC (1.2 mmol) at −60° for 15 min. Work-up as for **7** gave **19** (0.440 g 90%), NMR δ 2.4–0.6(47H, m), 0.2(9H, two singlets 1:1 for epimers). IR 2920, 1465, 1250, 1070, 840 cm^{-1}. MS. $C_{31}H_{56}OSi$ requires: 472–410, Obs: 472–410.

Cyclododecan - 1 - *oxiran* - 2 - *ylmethyltrimethylsilane* **20**. Cyclododecanone (0.728 g 4.0 mmol) was treated with CTC (8.0 mmol) at −55° for 0.5 Hr. Work-up as for **7** gave **20** (0.58 g 57% purified by preparative layer chromatography). NMR δ 2.6–2.2(19H, bm), 1.8–1.0(4H, bs), 0.1(9H, s). IR 2930, 2860, 1470, 1250, 840 cm^{-1}. (Found: C, 71.40; H, 11.70; $C_{16}H_{32}OSi$ requires: C, 71.64; H, 11.94%).

3 - O - *Methylestran* - 17 - *oxiran* - 20 - *ylmethyltrimethylsilane* **21**. Estrone - O - methylether (0.5 g 1.84 mmol) was treated with CTC (5.5 mmol) at −78° for 0.5 hr then warmed to 20° over 1.5 hr. Work-up as for **7** gave a thick oil (0.61 g) which was purified by preparative layer chromatography to give **21** (0.240 g 36%), m.p. 65°–70° [from ether-petroleum ether (b.p. 40–60°)]. NMR δ 6.9(1H, d J = 4 Hz), 6.5 (2H, d J = 12 Hz), 3.6(3H, s), 2.7(2H, bs), 1.3–2.2(14H, bm), 1.8(3H, s), 0.10 and 0.05 (9H, two singlets for epimers at C-20). IR (Numol mull) 2920, 1610, 1500, 1450, 1250, 1035, 860, 840 cm^{-1}. (Found: C, 74.30; H, 9.30. $C_{23}H_{34}O_2Si$ requires: C, 74.61; H, 9.24%).

2 - *Methylcyclohexan* - 1 - *oxiran* - 2 - *ylmethyltrimethylsilane* **22**. 2 - Methylcyclohexanone (2.0 g 17.8 mmol) was treated with CTC (26.7 mmol) at −78°, then warmed to 20° over 1.5 hr. Work-up as for **7** gave **22** (2.7 g 77%), b.p. 65°–68°/0.5 mm Hg. NMR δ 2.2(1H, s), 2.0(1H, s), 1.5 (9H, bs), 0.8–1.2 (3H, bm), 0.15(9H, s) and 0.10(9H, s) for two epimers. IR 2930, 2860, 1250, 840 cm^{-1}. MS. $C_{11}H_{22}OSi$ requires: 198.144, Obs: 198.144.

Bicyclo[2.2.1]*heptan* - 1 - *oxiran* - 2 - *ylmethyltrimethylsilane* **23**. Bicyclo[2.2.1] heptan - 1 - one (1.0 g 9 mmol) was treated with CTC (10.9 mmol) at −50° for 1 hr then warmed to 20° over 1 hr. Work-up as for **7** gave **23** (1.3 g 76%), b.p. 60° 0.05 mm Hg. NMR δ 2.5(1H, s), 2.2 (1H, s), 1.0–1.9(10H, m), 0.25(9H, s), and 0.1 (9H, s) for epimers. IR 2960, 1410, 1250, 845 cm^{-1}. MS. $C_{11}H_{22}OSi$ requires: 196–128, Obs: 196.128.

5 - *Isopropenyl* - 2 - *methylcyclohex* - 2 - *en* - 1 - *oxiran* - 2 - *ylmethyltrimethylsilane* **24**. Carvone (2.0 g 13.3 mmol) was treated with CTC (20.0 mmol) at −78° and warmed to 20° over 1.5 hr. Work-up as for **7** gave the crude product which was distilled to give **24** (76%), b.p. 75°–83°/0.4 mm. NMR δ 5.6(1H, bs), 4.6(2H, s), 1.8–2.5(6H, bm), 1.55(3H, s), 1.4(3H, bs), 0.15(9H, s). IR 2940, 2920, 1250, 860, 840 cm^{-1}. MS. $C_{14}H_{24}OSi$ requires: 236.159, Obs: 236.160.

Cycloheptan - 1 - *oxiran* - 2 - *ylmethyltrimethylsilane* **25**. Cycloheptanone (1.57 g 13.3 mmol) was treated with CTC (20.0 mmol) at −78° and warmed to 20° over 1.5 hr. Work-up as for **7**, gave **25** (1.5 g 58%), b.p. 60°/0.9 mm Hg. NMR δ 2.1(1H, s), 1.7(12H, bs), 0.2(9H, s). IR 2920, 1250, 840 cm^{-1}. MS. $C_{11}H_{22}OSi$ requires: 198.144, Obs: 198.144.

3 - *Methoxyandrosta* - 3,5 - *dien* - 17 - *oxiran* - 20 - *ylmethyltrimethylsilane* **26**. 3 - Methoxyandrosta - 3,5 - dien - 17 - one (1.0 g 3.3 mmol) was treated with CTC (9.9 mmol) at −78° for 1 hr then warmed to 20° over 1.5 hr. Work-up as for **5** gave the crude product which was purified by preparative layer chromatography to give **26** (0.520 g 41%). M.p. 58°–60° NMR δ 0.1(9H, s), 0.90(3H, s), 0.96(3H, s), 1.52(17H, m), 2.1 (1H, s), 3.45 (3H, s), 5.03(2H, m). (Found: C, 74.40; H, 9.6. $C_{24}H_{38}O_2Si$ requires: C; 74.61; H, 9.84%).

10 - *Oxoanthracen* - 9 - *oxiran* - 2 - *ylmethyltrimethylsilane* **27**. Anthraquinone (0.5 g 2.4 mmol) was treated with CTC (5 mmol) at −78° for 0.5 hr then warmed to 20° over 1 hr. Work-up as for **5** gave **27** (0.740 g 89%), m.p. 113.5°–115° (from CH_2Cl_2–hexane). NMR δ 8.1–8.4(2H, m), 7.4–7.6(6H, m), 2.5(1H, s), 0.0(9H, s). IR (Nujol mull) 2940, 2920, 1710, 1600, 1590, 1300, 1275, 1250, 850, 840, 760, 750 cm^{-1}. (Found: C, 73.55; H, 6.24. $C_{18}H_{18}O_2Si$ requires: C, 73.40; H, 6.12%).

Bis-adduct from [2.2]-*paracyclophane*-1,10-*dione*.[27] The dione (50 mg 0.21 mmol) was treated with CTC (0.89 mmol) at −78° for 1 hr then warmed to 20° over 1 hr. Work-up gave **28** (77 mg 89%) purified by preparative layer chromatography. NMR δ 6.1–6.7(8H, m), 3.0(1H, bs), 2.5(1H, bs), 1.2(4H, bs), 0.3(9H, s), 0.0(9H, s) for epimers. IR 2960, 2920, 2850, 1460, 1380, 1250, 840 cm^{-1}. MS. $C_{24}H_{32}O_2Si_2$ requires: 408.194, Obs: 408.195.

Hydrolysis of α,β-epoxytrimethylsilanes

Compound **5**(0.20 g) in 10% aqueous MeOH (5 ml) was stirred at −5° and $BF_3{\cdot}OEt_2$ (0.095 ml) added. The mixture was warmed to 20° and after 2 hr poured into 0.5 M HCl (20 ml) and extracted with CH_2Cl_2 (3 × 20 ml). Drying ($MgSO_4$) and evaporation gave *phenylacetaldehyde dimethylacetal* (0.14 g 82%).[28]

Compound **5** (0.19 g) in 20% aqueous THF (2 ml) was stirred at 20° and 70% $HClO_4$ (0.01 ml) added. After 4 hr the mixture was poured into water (20 ml), extracted with CH_2Cl_2 (3 × 20 ml), dried ($MgSO_4$) and evaporated *in vacuo* at 30° to give *phenylacetaldehyde* (0.14 g 85%), 2,4-DNP m.p. 230–235° (from ether–petroleum ether).[29]

Compound **8** (2.8 g) in 20% aqueous THF (20 ml) was treated with 70% $HClO_4$ (1 ml) as above, and worked-up to give *undecanal* (1.76 g 85%).[30]

Compound **10** (0.25 g) in 20% aqueous THM (5,ml) was treated with 60% $HClO_4$ (0.1 ml) as above, and worked-up to give 2-(6,6 - *Dimethylbicyclo*[3.1.1]*hept* - 2 - *ene*)*acetaldehyde* (180 mg 94%). IR 1700, 1610 cm^{-1}. NMR δ 0.8(3H, s), 1.3(3H, s), 2.0–2.4(8H, m), 6.6(1H, b), 9.7(1H, t J = Hz).[31]

Compound **12** (0.18 g) in 20% aqueous THF (3 ml) was treated with 70% $HClO_4$ (0.1 ml), as above, to give *cyclohexane carboxaldehyde* (0.08 g 74%), 2,4-DNP m.p. 169°–171° (from EtOAc/petroleum ether).[32]

Compound **13** (0.20 g) in 90% formic acid (1 ml) at 20° was stirred for 0.5 hr and the mixture evaporated to give 2-*adamantane carboxaldehyde* (0.10 g 71%), m.p. 99°–102°.[33]

Compound **17** (0.375 g) in 20% aqueous THF (4 ml) was treated with 70% $HClO_x$ (0.5 ml) as above to give 4 - *t* - *butylcyclohexylcarboxaldehyde* (0.188 g 72%). NMR δ 9.8 and 9.7 (two singlets 2:1 for epimers), 2.4–0.7(10H, m), 0.85 and 0.75(9H, two singlets).[34]

Compound **21** (50 mg) in 90% formic acid (2 ml) was stirred at 20° for 0.5 hr. Evaporation (0.05 mm Hg) gave a solid which was purified by preparative layer chromatography to give 3 - *methoxy* - 17β - *formyl* - 1,3,5 - *estratriene* (38 mg 98%), m.p. 110°–112°. IR (Nujol) 2920, 2700, 1710, 1610, 1400, 1250 cm^{-1}. NMR 0.7(3H, s), 1.1–2.4 (14H, bm), 2.7(2H, bs), 3.6(3H, s), 6.2–7.9(3H, m), 9.6(1H, s). (Found: C, 80.42, H, 8.96. $C_{20}H_{26}O_2$ requires: C, 80.53; H, 8.72%).

Compound **22** (0.90 g) in 90% formic acid (3 ml) was stirred at 20° for 0.5 hr to give 2 - *methylcyclohexyl carboxaldehyde* (0.44 g 77%), b.p. 80°/0.5 mm Hg.[35] Compound **23** (500 mg) in 20% aqueous THF (10 ml) was treated with 70% $HClO_4$ (0.5 ml) for 10 hr at 20°. Work-up gave 3 - *formyl* - *bicyclo*[2.2.1]*heptane* (0.23 g 73%) as a mixture of epimer (3.6:1). NMR 1.1–2.0(6H, bm), 2.1–2.4(2H, bm), 2.6(2H, bs), 3.6(1H, bm), 9.5(1H, s) and 9.6(1H, s).[36]

The epoxytrimethylsilane **23** (0.5 g) in 90% formic acid (2 ml) was stirred at 20° for 0.5 hr. Evaporation and crystallization gave bicyclo[3.2.1]octan-2-one **35** m.p. 127–129°.[18]

Compound **24** (0.5 g) in 20% aqueous THF (6 ml) was treated

with 70% $HClO_4$ (0.5 ml) for 2 hr at 20°. Work-up gave a liquid (0.270 g 78%) b.p. 85°/0.4 mm Hg. NMR δ 1.7(6H, s), 1.9(2H, s), 2.1(5H, bs), 4.6(2H, d, J = 5 Hz), 5.6(1H, bs), 10.0(1H, s). About 35% of the deconjugated aldehyde was present. IR 2920, 2860, 1710, 1660, 1635, 1440, 1370, 1230, 890, 810, 790, 760 cm^{-1}. MS. $C_{11}H_{16}O$ requires: 164.120, Obs: 164.120.

Compound **25** (0.5 g) in 90% formic acid (3 ml) was stirred at 20° for 1 hr. Work-up gave *cycloheptane carboxaldehyde* (0.28 g 88%).[37]

All the above aldehydes were formed in ≥95% purity directly from the hydrolysis reaction.

Cyclohexanecarboxaldehyde ethyleneacetal **36** (X = Y = 0, n = 2). **12** (0.200 g) in benzene (2 ml) was treated with *p*-toluenesulfonic acid monohydrate (0.02 g) and ethylene glycol (0.07 ml). The mixture was heated at reflux for 2 hr, poured into sat $NaHCO_3$aq, and extracted with ether (2 × 10 ml). The dried ($MgSO_4$) extract was evaporated to give **36** (X = Y = 0, n = 2) (0.14 g 80%) b.p. 80°/0.25 mm Hg. NMR δ 4.5(1H, m), 3.8(4H, bs), 1.0–1.9(11H).[38]

Cyclohexanecarboxaldehyde dithioethyleneacetal **36** (X = Y = S, n = 2). **12** (0.200 g) was treated as above, except 1,2-ethanedithiol was used; **36** (X = Y = S, n = 2) (0.17 g 78%), b.p. 85°/0.25 mm Hg. NMR δ 4.2(1H,m), 3.0(4H, bs), 1.0–2.0(11H).

Cyclohexanecarboxaldehyde hemithioethyleneacetal **36** (X = S, Y = 0, n = 2). **12** (0.200 g) was treated as above, except 2-thioethanol was used; **36** (X = S, Y = 0, n = 2) (0.138 g 70%). NMR δ 3.1(1H, m), 2.6(1H, m), 1.0–2.0(11H).

Cyclohexanecarboxaldehyde 1,3-*dithiopropyleneacetal* **36** (X = Y = S, n = 3). **12** (0.200 g) was treated as above, except 1,3-propanedithiol was used; **36** (X = Y = S, n = 3) (0.150 g 65%). NMR δ 4.0(1H, m), 2.5–3.0(6H, m), 1.0–2.0(11H).

Cyclohexane carboxylic acid from **12**. **12** (1. g) in glacial AcOH (2 ml) was treated with 30% H_2O_2 (4 ml) and conc H_2SO_4 (2 drops). After 72 hr at 20° the mixture was poured into sat $NaHCO_3$aq and extracted with ether. The aqueous layer was acidified (2NHCl), extracted with ether (2 × 10 ml), dried ($MgSO_4$) and evaporated to give cyclohexane carboxylic acid (0.44 g 65%), m.p. 27°–29°.

Cyclohexan - 1 - oxiran - 2 - ylmethyl - 2 - methyltrimethylsilane **38**. **12** (0.20 g) in dry pentane (10 ml) was treated with t-BuLi (0.88 ml of a 1.85 M soln in pentane) at −78°, followed by TMEDA (0.25 ml). After 1 hr at −78° MeI (1 ml) was added and the mixture warmed to 20° over a period of 0.5 hr. Work-up in the usual way gave **38** (0.19 g 88%), b.p. 60°/0.125 mm Hg. NMR δ 0.0(9H, s), 1.25(3H, s), 1.5(10H, b). MS. $C_{11}H_{22}OSi$ requires: 198.144. Obs: 198.144. Identical to an authentic sample prepared from cyclohexanone and $Me_3SiCliMeCl$.[38]

Cyclohexan - 1 - oxiran - 2 - ylmethyl - 2 - allyltrimethylsilane **39**. To a soln of **37** (prepared as above) was added allylbromide (0.28 ml) at −78°. Work-up gave **39** (0.17 g 70%), b.p. 65°/0.08 mm Hg. IR 2920, 2865, 1635, 1250, 845 cm^{-1}. NMR δ 0.1(9H, s), 1.2(2H, d J = 3.5 Hz), 1.55(10H, bs), 4.8–5.2(2H,m), 5.3–6.0(1H,m). MS. $C_{13}H_{24}OSi$ requires: 224.160. Obs: 224.160.

Cyclohexan - 1 - oxiran - 2 - ylmethyl - 2,2 - bis - trimethylsilane **40**. To a soln of **37** (prepared as above) was added chlorotrimethylsilane (0.18 ml) at −78°. Work-up gave **40** (0.16 g 60%), b.p. 65°/0.13 mm Hz. IR 2940, 1450, 1250, 845 cm^{-1}. NMR δ 0.25(18H, s), 155(10H, b). MS. $C_{13}H_{28}OSi_2$ requires: 256.162. Obs: 256.163.

Latia Luciferin **41**. Dihydro-β-ionone[23] (0.3 g 1.55 mmol) was treated with CTC (2.0 equiv) at −78° for 0.5 hr then warmed to 20°. Work-up in the usual way gave **42** (0.37 g 85%), b.p. 90°/0.15 mm Hg. NMR δ 0.1(9H, s), 0.75–1.10 (9H, m), 1.20–1.45(7H,m), 1.50–1.55(3H, bs), 1.80–1.85(2H, bs), IR 2950, 2920, 2900, 1250, 845 cm^{-1}. MS. $C_{17}H_{32}OSi$ requires: 280.222. Obs: 280.222.

Compound **42** (0.200 g 0.7 mmol) in dry formic acid (freshly distilled form boric anhydride) was stirred at 20° for 0.5 hr. Evaporation under vacuum gave **41** (0.150 g 95%)[22] after chromatography over florisil, eluting with hexane. NMR δ 7.97(1H, s), 7.92(1H, s for *cis*-isomer *ca.* 10%), 6.96(1H, bs), 1.73(3H, d J = 1.5 Hz), 1.60(3H, bs), 1.0(6H, s).

Mixture contains *ca.* 10% *of the cis*-isomer.

Cyclohexan - 1 - oxiran - 2 - ylmethyl - dimethylphenylsilane **46**. Chloromethyldimethylphenylsilane (2.20 ml 12.2 mmol) in THF (15 ml) at −78° was treated with s-BuLi (8.73 ml of a 1.4 M soln in hexane). After 15 min at −55° the soln was cooled to −78 and cyclohexanone (1.05 ml) added. The mixture was warmed to 0° and poured into sat NH_4Claq, and extracted with ether (2 × 30 ml). Drying ($MgSO_4$) and evaporation gave **46** (2.8 g). Distillation gave pure **46** (1.1 g 50%), b.p. 90°–92° 10.05 mm Hg. NMR δ 0.25(6H, s), 1.35(10H, s), 1.9(1H, s), 7.05–7.40(5H, m), IR 2920, 1450, 1430, 1410, 1250, 1115, 890, 840, 820 cm^{-1}. MS. $C_{15}H_{22}OSi$ requires: 246.144. Obs: 246.144.

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