Regiospecific Conversion of Oxiranes, Oxetanes, and Lactones into Difunctional Nitrogen Compounds *via* Aminosilanes and Aminostannanes

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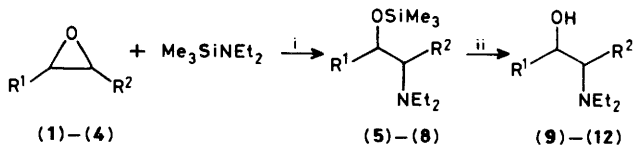
The insertion reactions of diethylaminotrimethylsilane (TMSDEA) and diethylaminotrimethylstannane (TMSnDEA) into oxirane, oxetane, and lactone rings are reported. Regioisomerically pure β- and γ-amino alcohols were obtained, with $AlCl_3$ or Et_2AlCl catalysis, from monoalkyloxiranes and monoalkyl- and aryl-oxetanes respectively, whereas, in the majority of cases, reactions involving polysubstituted oxiranes resulted in a loss of regioselectivity. Ring-opening reactions of the lactone rings with TMSDEA led, on the other hand, to β-amino acids or to ω-hydroxyamides depending upon the ring size.

With TMSnDEA, spontaneous ring cleavage of the alkyloxiranes and of β-propiolactone occurred with reversed regioselectivity, while the oxetanes and γ- and δ-lactones were opened with the same regiochemistry as that found with TMSDEA for the same ring systems.

A major aim in organic synthesis is to find a short, regioselective synthesis of difunctional compounds and many different routes have been proposed. Of these, the use of organometallics for the ring-opening of saturated heterocyclic ring systems which are activated by strain or electronic effects is of particular interest.[1]

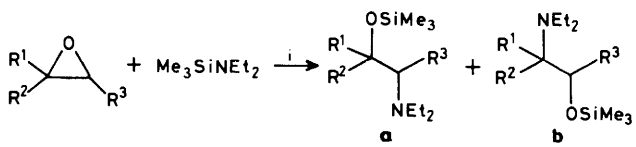
In previous papers we showed that the ring-opening reactions of simple oxiranes,[2] thiiranes,[2] and saturated lactones[4] by group 4b organometallics occurs in a regioselective fashion leading to difunctional β-amino and β-mercapto compounds and to ω-hydroxyamides.

In this paper we report a much more comprehensive screening of saturated heterocyclic ring functionalisation through group 4b organometallics, which demonstrates the potential and possible limitations of this synthetically attractive strategy and shows the possibility, in many cases of controlling the regioselectivity of the synthesis by simply changing the organometallic reagent or the ring system. Diethylaminotrimethylsilane (TMSDEA) and diethylaminotrimethylstannane (TMSnDEA), which are readily available, versatile organometallic reagents, were employed for the regioselective ring opening of cyclic ethers and esters in an attempted preparation of difunctional amino compounds.



(1), (5), (9) R^1 = Me, R^2 = H
(2), (6), (10) R^1 R^2 = C_4H_8
(3), (7), (11) R^1 = Me, R^2 = Ph
(4), (8), (12) R^1 = $PhOCH_2$, R^2 = H

Scheme 1. Reagents: i, Lewis acid; ii, H^+



	a : b
(13), (16) R^1 = H, R^2 = Et, R^3 = Me	45:55
(14), (17) R^1 = Ph, R^2 = R^3 = H	70:30
(15), (18) R^1 = R^2 = R^3 = Me	30:70

Scheme 2. Reagents: i, $AlCl_3$

Results and Discussion

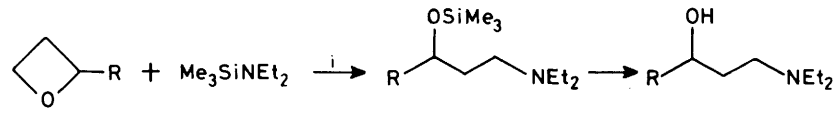
Reactions with Aminosilanes.—The oxiranes (**1**)—(**4**) reacted with TMSDEA in boiling CH_2Cl_2 in the presence of catalytic amounts of a Lewis acid, affording reasonable yields of the β-trimethylsiloxyamines (**5**)—(**8**) (Scheme 1). The best results were obtained with catalytic amounts (10%) of $AlCl_3$ or Et_2AlCl, while $ZnBr_2$, $ZnCl_2$, $SnCl_4$, $TiCl_4$, or BF_3·Et_2O gave little or none of the insertion products.

Compounds (**5**)—(**8**) were easily isolated by fractional distillation and gave the corresponding β-amino alcohols (**9**)—(**12**) on treatment with gaseous HCl in dry Et_2O.

The regiochemistry of the reaction was reduced with sterically hindered or phenyl substituted oxiranes and varying amounts of the other possible insertion product were obtained. 3-Ethyl-2-methyloxirane (**13**), 2-phenyloxirane (**14**), and 2,2',3-trimethyloxirane (**15**), under identical reaction conditions, afforded, in fact, compounds (**16**)—(**18**) as a mixture of the two possible regioisomers (Scheme 2).

The relative amounts of (**16a**) and (**16b**), (**17a**) and (**17b**), and (**18a**) and (**18b**) were estimated by g.l.c.–mass spectral analysis, no attempts being made to separate the products. Their regiochemistry was established mainly on the grounds of a fragmentation pattern typical for tertiary amines.[5] An accurate g.l.c.–mass spectral analysis of all the reaction mixtures previously reported also showed that varying amounts of α,β-elimination products and β-chlorosiloxy derivatives were formed; the former resulted from deprotonation induced by the nitrogen base, while the latter, detected only when $AlCl_3$ was used as the catalyst, were probably formed owing to the presence of HCl in the Lewis acid.

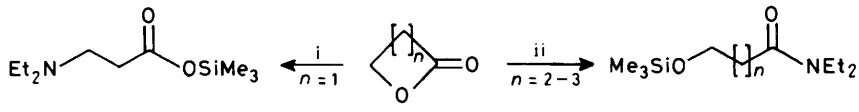
With compounds (**2**), (**3**), and (**14**), the elimination products were formed in 5—15% yield; only (**2**) and (**4**) gave small amounts (< 5%) of the β-chloro derivative. No by-products were detected with Et_2AlCl which was found to be a very good



(19)–(21) (22)–(24) (25)–(27)

(19), (22), (25) R = H
(20), (23), (26) R = Me
(21), (24), (27) R = Ph

Scheme 3. *Reagents:* i, 10% $AlCl_3$



(29) (28) n = 1 (32) n = 2
(30) n = 2 (33) n = 3
(31) n = 3

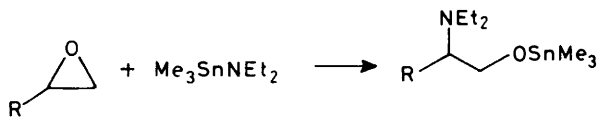
Scheme 4. *Reagents:* i, Me_3SiNEt_2; ii, Me_3SiNEt_2, $AlCl_3$

catalyst in the ring-opening of compound (**1**), but gave smaller amounts of the insertion product with the more substituted oxiranes (**2**), (**4**), (**13**), and (**14**), and did not promote any reaction with compounds (**3**) and (**15**).

The same pattern of reactivity was observed with the less strained oxetanes (**19**)—(**21**) which were easily transformed with TMSDEA–$AlCl_3$ into the corresponding γ-siloxyamines (**22**)—(**24**) and then converted in high yields into the γ-amino alcohols (**25**)—(**27**) (Scheme 3). Complete regioselectivity and no α,β-elimination were the main features of this reaction.

A ring cleavage was also observed with the cyclic esters, but in this case the regioselectivity changed as the ring size increased. Whereas β-propiolactone (**28**) reacted, in the absence of a catalyst, with TMSDEA to give the β-siloxyamino acid (**29**), the less strained lactones (**30**)—(**31**) gave, under $AlCl_3$ catalysis, the ω-siloxyamides (**32**)—(**33**) as shown in Scheme 4.

Reactions with Aminostannanes.—We have recently reported[2] that the oxiranes (**1**), (**2**), and (**14**) undergo a regiospecific ring cleavage with organotin compounds such as TMSnDEA, following the pattern shown below.



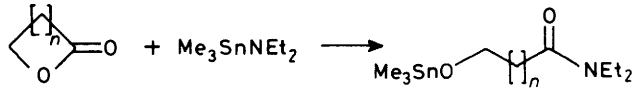
The stannylated adduct results from the nucleophilic attack of the amino group on the most substituted carbon atom of the ring, with the opposite regioselectivity to that observed with the corresponding aminosilane.

Even though the reaction of simple oxiranes with TMSnDEA takes place completely regiospecifically, this organometallic reagent appears to be much less versatile than TMSDEA in that it does not cleave the more sterically hindered oxiranes (**3**), (**13**) and (**15**), even in the presence of a Lewis acid which interacts directly with the stannylated reagent.

Surprisingly the oxirane (**4**) gave the adduct (**34**), which was then transformed into the β-amino alcohol (**12**) obtained from (**4**) with $AlCl_3$ and TMSDEA (Scheme 5). It is probable that assistance from the ethereal oxygen in the side chain is responsible for this unexpected reactivity.

On the other hand, TMSnDEA underwent insertion into the oxetane ring (Scheme 6) giving the γ-stannoxyamines (**35**) and (**36**) under different conditions, the yields decreasing (see Experimental section) on changing R from H to methyl. 2-Phenyloxetane (**21**) gave no insertion product. With these four-membered cyclic ethers no change of regioselectivity was noticed on changing the group 4b element from Si to Sn and the oxetane ring cleavage occurred through the same nucleophilic attack of the amino group on the less substituted carbon as that observed with TMSDEA–$AlCl_3$.

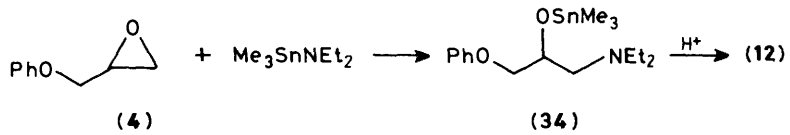
Finally, cyclic esters undergo regioselective ring cleavage giving products resulting from nucleophilic attack of the NEt_2 moiety at the carbonyl carbon,[4] as shown below.



n = 1,2,3,4

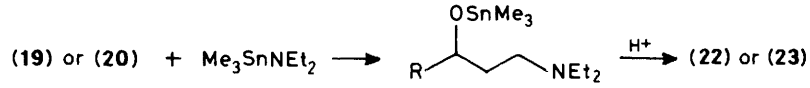
Of the relevant features of ring-opening reactions by group 4b organometallics previously described, the change in the regioselectivity of the insertion reactions occurring in many cases on moving from silicon to tin derivatives is of major interest. The different nature of the heterocyclic rings investigated and the various experimental conditions employed make it difficult to find a general mechanistic scheme covering all the reactions studied so far. However, several general aspects of the above reactions can be outlined even at this preliminary stage.

Thus, the ring opening of cyclic ethers by aminosilanes can be related to the S_N-type cleavage of these rings: nucleophilic attack of the amino group of TMSDEA leads, in fact, to secondary amino alcohols in the case of monosubstituted oxiranes and oxetanes. The exception to this rule, the phenyl substituted oxirane, shows, on the other hand, that in the presence of even a slightly electron attracting group, competitive attack can take place; thus it seems that the overall reaction depends on a subtle balance between the electronic and steric factors. Further support for this suggestion comes from the reaction of 2-methyl-3-phenyloxirane (**3**) with TMSDEA where, when the steric hindrance at both C-2 and C-3 is increased, the attack at the more electronically activated position is favoured to such an extent that it again gives only



(4) (34)

Scheme 5.



(35) R = H
(36) R = Me

Scheme 6.

one regioisomer. The role played by the Lewis acid catalyst in these reactions cannot simply be to interact with the ring heteroatom, since this would result in a different regioselectivity. The possibility that an exchange reaction between the Lewis acid and TMSDEA might lead to a nitrogen–aluminium compound[6] which, as previously reported, could interact as a nucleophile,[7] cannot be completely ruled out.

On the other hand, the more developed metallic character of Sn in the aminotin derivative TMSnDEA makes it more plausible that this organometallic reagent might act as an internal Lewis acid: its interaction with the oxygen, followed by nucleophilic attack at the more stabilised carbocationic centre by the NEt_2 framework, might account for the formation of the primary amino alcohols together with an electronically assisted nucleophilic cleavage of the oxirane ring. Unfortunately the lack of reactivity of the disubstituted oxiranes (**3**), (**13**), and (**15**) with TMSnDEA and the very precise reaction conditions required for the conversion of the oxetanes (**20**) and (**21**) suggests that TMSnDEA is greatly affected by steric hindrance; this, coupled with the impossibility of using a Lewis acid catalyst in the presence of TMSnDEA, prevented us from obtaining a more complete picture of the reaction of this organometallic reagent with cyclic ethers.

Despite the fact that the mechanistic aspects have still to be clarified, the high yields, the simplicity, and the high regioselective control of this ring-opening reaction of oxiranes, oxetanes, and saturated lactones by group 4b organometallic reagents, make it a unique synthetic route to difunctional organic molecules, and it is worthy of further development.

Experimental

I.r. spectra were recorded on a Perkin-Elmer 283 spectrophotometer for liquid films; n.m.r. spectra were obtained with a Perkin-Elmer R32 (90 MHz) spectrometer for $CDCl_3$ solutions, with Me_4Si as internal standard; g.l.c.–mass spectroscopic (g.c.—m.s) analyses were performed with a Varian Matt 113 instrument connected to a Varian 3400 aerograph equipped with a SE-30, 12-m capillary column. CH_2Cl_2 used was dried and free from ethanol. TMSDEA and TMSnDEA were prepared by the methods of Itoh[8] and Lappert,[9] respectively. The amino alcohols (**9**), (**10**), (**12**), and (**25**)—(**27**) were identified by comparison with the physical and spectroscopical features described in the literature.[10–15]

Ring Cleavage of Oxiranes with TMSDEA–Lewis Acid.—*2-Methyloxirane* (**1**). To a solution of 2-methyloxirane (**1**) (0.58 g, 10 mmol) and TMSDEA (1.45 g, 10 mmol) at 0 °C in dry CH_2Cl_2 (4 ml), $AlCl_3$ (0.13 g, 1 mmol) was rapidly added and the mixture was refluxed for 2 h. After evaporation of the solvent, the residue was treated with pentane and the resulting solid was filtered off. The pentane was then evaporated from the filtrate and fractional distillation gave 1-*diethylamino*-2-*trimethylsiloxypropane* (**5**) (1.66 g, 68%), b.p. 56—58 °C at 7.5 mmHg. Data in Table 1.

1-*Oxabicyclo*[4.1.0]*heptane* (**2**). Compound (**2**) was treated as for (**1**); after the mixture had been boiled for 20 h, g.c—m.s showed an 80% yield of conversion products. Fractional distillation gave 2-*diethylamino*-1-*trimethylsiloxycyclohexane* (**6**) (1.04 g, 43%), b.p. 95—98 °C at 1.5 mmHg. Data in Table 1.

3-*Methyl*-2-*phenyloxirane* (**3**). Compound (**3**) was treated as for (**1**); after the mixture had been boiled for 8 h, fractional distillation gave 1-*diethylamino*-1-*phenyl*-2-*trimethylsiloxypropane* (**7**) (1.42 g, 51%), b.p. 83—85 °C at 1.5 mmHg. Data in Table 1.

2-*Phenoxymethyloxirane* (**4**). Compound (**4**) was treated as for (**1**); after 15 h at room temperature, fractional distillation gave 3-*diethylamino*-1-*phenoxy*-2-*trimethylsiloxypropane* (**8**) (1.51 g, 51%), b.p. 100—101 °C at 0.03 mmHg. Data in Table 1.

2-*Ethyl*-3-*methyloxirane* (**13**). Compound (**13**) was treated similarly; after the mixture had been boiled for 8 h, g.c.—m.s. showed a complete conversion of the starting reagent into 2-*diethylamino*-3-*trimethylsiloxy* (**16a**) (45%) and 3-*diethyl*-2-*trimethylsiloxypentane* (**16b**) (55%). Mass spectrum: (**16a**) *m/z* 231 (M^+), 114 (base), and 73; (**16b**) *m/z* 231 (M^+), 100 (base), and 73.

2-*Phenyloxirane* (**14**). Compound (**14**) was treated similarly; after 3 h at room temperature, g.c.—m.s. showed complete conversion of the starting reagent into 1-*diethylamino*-2-*trimethylsiloxy* (**17a**) (70%) and 2-*diethylamino*-1-*trimethylsiloxy*-2-*phenylethane* (**17b**) (30%). Mass spectrum: (**17a**) *m/z* 265 (M^+), 162 (base), and 73; (**17b**) *m/z* 265 (M^+), 86 (base), and 73.

2,2,3-*Trimethyloxiran* (**15**). After 18 h at room temperature, g.c.—m.s. showed 85% conversion into the product, containing 2-*diethylamino*-3-*trimethylsiloxy*-(**18a**) (30%) and 3-*diethylamino*-2-*trimethylsiloxy*-3-*methylbutane* (**18b**) (70%), and the β-chlorosiloxy derivative (5%). Mass spectrum: (**18a**) *m/z* 216 ($M^+ - 15$), 114 (base), and 73; (**18b**) *m/z* 216 ($M^+ - 15$), 100 (base), and 73.

Ring Cleavage of Oxetanes with TMSDEA–Lewis Acid.—*Oxetane* (**19**). To a solution of oxetane (**19**) (0.59 g, 10 mmol) and TMSDEA (1.45 g, 10 mmol) at −78 °C in dry CH_2Cl_2 (6 ml), $AlCl_3$ (0.13 g, 1 mmol) was rapidly added and the mixture maintained at room temperature for 12 h. Evaporation of the solvent and fractional distillation gave 1-*diethylamino*-3-*tri-*

Table 1. Ring-opening of oxiranes and oxetanes with TMSDEA and TMSnDEA

Starting ethers	Organomet. reagent.	Percentage conversion		Products	Yield (%)	*m/z*	δ (p.p.m.)
		$AlCl_3$	Et_2AlCl				
(**1**)	TMSDEA	100	100	(**5**)	68	203 (M^+), 114 (base)	0.08 (9 H, s, $SiCH_3$), 1.1 (6 H + 3 H, m, $EtCH_3$ + CH_3CO), 2.5 (4 H + 2 H, m, $EtCH_2$), 3.7 (1 H, m, OCH)
(**2**)	TMSDEA	80	23	(**6**)	43	243 (M^+), 112 (base)	0.10 (9 H, s, $SiCH_3$), 1.0—1.4 (8 H + 6 H, CH_2-cyclohex. + $EtCH_3$), 2.4—2.8 (4 H + 1 H, m, $EtCH_2$ + NCH), 3.6 (1 H, m, OCH)
(**3**)	TMSDEA	95	2	(**7**)	51	269 (M^+), 162 (base)	0.06 (9 H, s, $SiCH_3$), 1.20 (6 H, t, *J* 6 Hz, $EtCH_3$), 1.40 (3 H, d, *J* 8 Hz, CH_3CO), 2.2—2.9 (4 H, m, $EtCH_2$), 3.71 (1 H, d, *J* 9 Hz, NCH), 4.5 (1 H, m, OCH), 7.6 (5 H, m, ArH)
(**4**)	TMSDEA	100	10	(**8**)	51	307 (M^+), 204 (base)	0.10 (9 H, s, $SiCH_3$), 1.05 (6 H, t, *J* 6 Hz, $EtCH_3$), 2.6 (4 H + 2 H, m, $EtCH_2$ + NCH_3), 3.9—4.5 (2 H + 1 H, m, OCH_2 + OCH), 7.2 (3 H, m, ArH), 7.5 (2 H, m, ArH)
(**19**)	TMSDEA	70	60	(**22**)	41	203 (M^+), 73 (base)	0.10 (9 H, s, $SiCH_3$), 1.04 (6 H, t, *J* 6 Hz, $EtCH_3$), 1.7 (2 H, m, CCH_2C), 2.5 (4 H + 2 H, m, $EtCH_2$ + NCH_2), 3.55 (2 H, t, *J* 6 Hz, OCH_2)
(**20**)	TMSDEA	75	55	(**23**)	43	217 (M^+), 128 (base)	0.12 (9 H, s, $SiCH_3$), 1.05 (6 H, t, *J* 6 Hz, $EtCH_3$), 1.18 (3 H, d, *J* 7 Hz, CCH_3) 2.2 (2 H, m, CCH_2C), 2.6 (4 H + 2 H, m, $EtCH_2$ + NCH_2), 3.7 (1 H, m, OCH)
(**21**)	TMSDEA	traces	80	(**24**)	56	279 (M^+), 206 (base)	0.18 (9 H, s, $SiCH_3$), 1.20 (6 H, t, *J* 6 Hz, $EtCH_3$), 2.0 (2 H, m, CCH_2C), 2.5 (4 H + 2 H, m, $EtCH_2$ + NCH_2), 4.81 (1 H, t, *J* 5 Hz, OCH), 7.5 (5 H, m, ArH)
(**4**)	TMSnDEA			(**34**)	70		0.30 (9 H, s, $SnCH_3$), 1.05 (6 H, t, *J* 6 Hz, $EtCH_3$), 2.7 (4 H + 2 H, m, $EtCH_2$ + NCH_2), 3.9—4.3 (2 H + 1 H, m, OCH_2 + OCH), 7.1 (3 H, m, ArH), 7.5 (2 H, m, ArH)
(**19**)	TMSnDEA			(**35**)	35		0.30 (9 H, s, $SnCH_3$), 1.10 (6 H, t, *J* 6 Hz, $EtCH_3$), 1.7 (2 H, m, CCH_2C), 2.5 (4 H + 2 H, m, $EtCH_2$ + NCH_2), 3.45 (2 H, t, *J* 6 Hz, OCH_2)
(**20**)	TMSnDEA			(**36**)	31		0.31 (9 H, s, $SnCH_3$), 1.05 (6 H, t, *J* 6 Hz, $EtCH_3$), 1.20 (3 H, d, *J* 7 Hz, CCH_3), 1.8 (2 H, m, CCH_2C), 2.4 (4 H +2 H, m, $EtCH_2$ + NCH_2), 3.5 (1 H, m, OCH)

* Elemental analyses (C, H) for all compounds were within ± 0.4% of the calculated values and have been deposited as a supplementary publication [Sup. No. 56033 (2 pp.)]. For details of the supplementary publications scheme see Instruction for Authors (1984), *J. Chem. Soc., Perkin Trans. 1*, 1984, Issue 1.

methylsiloxypropane (**22**) (0.83 g, 41%), b.p. 66—68 °C at 3.8 mmHg. Data in Table 1.

2-*Methyloxetane* (**20**). Compound (**20**) was treated as for (**19**); after the mixture had been boiled for 3 h, fractional distillation gave 1-*diethylamino*-3-*trimethylsiloxybutane* (**23**) (0.98 g, 45%), b.p. 65—68 °C at 3.8 mmHg. Data in Table 1.

2-*Phenyloxetane* (**21**). Following the same procedure, 1-*diethylamino*-3-*phenyl*-3-*trimethylsiloxypropane* (**24**) was obtained exclusively with Et_2AlCl as the Lewis acid catalyst. After evaporation of the solvent and fractional distillation we obtained the *product* (**24**) (1.55 g, 56%), b.p. 104—106 °C at 0.38 mmHg. Data in Table 1.

Ring Cleavage of Lactones with TMSDEA.—β-*Propiolactone* (**28**). A solution of β-propiolactone (**28**) (0.72 g, 10 mmol) and TMSDEA (1.45 g, 10 mmol), in dry CH_2Cl_2 (4 ml) was refluxed for 4 h. After evaporation of the solvent and fractional distillation we obtained the trimethylsilyl ester of N,N-*diethylamino*-β-*alanine* (**29**) (1.57 g, 78%), b.p. 81—83 °C at 1.9 mmHg. Data in Table 2.

γ-*Butyrolactone* (**30**). To a solution of γ-butyrolactone (**30**) (0.5 g, 5.8 mmol) and TMSDEA (0.84 g, 5.8 mmol) at 0 °C in dry CH_2Cl_2 (5 ml), $AlCl_3$ (0.07 g, 0.6 mmol) was rapidly added and the mixture was refluxed for 10 h. After cooling, pentane was added, and the residue was filtered off; after evaporation of the solvent from the filtrate, fractional distillation gave N,N-*diethyl*-3-*trimethylsiloxybutyramide* (**32**) (0.8 g, 60%), b.p. 81—83 °C at 0.22 mmHg. Data in Table 2.

δ-*Valerolactone* (**31**). Following the same procedure as for (**30**), after the mixture had been boiled for 24 h and treated with

Table 2. Ring-opening reaction of lactones with TMSDEA

Starting compounds	$AlCl_3$ (% mol)	Products	Yield (%)	δ(p.p.m.)
(**28**)		(**29**)	78	0.10 (9 H, s, $SiCH_3$), 1.05 (6 H, t, *J* 7 Hz, $EtCH_3$), 2.5 (4 H + 2 H + 2 H, m, $EtCH_2$ + NCH_2 + $CH_2C{=}O$)
(**30**)	10	(**32**)	60	0.07 (9 H, s, $SiCH_3$), 1.1 (6 H, m, $EtCH_3$), 1.8 (2 H, m, CCH_2C), 2.3 (2 H, m, $CH_2C{=}O$), 3.3 (4 H, m, $EtCH_2$), 3.60 (2 H, t, *J* 6 Hz, OCH_2)
(**31**)	10	(**33**)	51	0.10 (9 H, s, $SiCH_3$), 1.2 (6 H, m, $EtCH_3$), 1.7 (4 H, m, CCH_2C), 2.2 (2 H, m, $CH_2C{=}O$), 3.3 (4 H, m, $EtCH_2$), 3.6 (2 H, t, *J* 6 Hz, OCH_2)

* See footnote, Table 1.

pentane, fractional distillation gave N,N-*diethyl*-4-*trimethylsiloxyvaleramide* (**33**) (0.58 g, 40%), b.p. 90—92 °C at 0.07 mmHg. Data in Table 2.

Ring Cleavage of Oxiranes with TMSnDEA.—*2-Phenoxymethyloxirane* (**4**). A solution of 2-phenoxymethyloxirane (**4**) (1.50 g, 10 mmol) and TMSnDEA (2.70 g, 10 mmol) in dry CH_2Cl_2 (6 ml) was refluxed for 12 h. After evaporation of the solvent, fractional distillation gave 3-diethylamino-1-phenoxy-2-trimethylstannoxypropane (**34**) (2.94 g, 70%), b.p. 121—123 °C at 0.04 mmHg.

Ring Cleavage of Oxetanes with TMSnDEA Oxetane (**19**).—A solution of oxetane (**19**) (0.58 g, 10 mmol) and TMSnDEA (2.32 g, 10 mmol) in dry CH_2Cl_2 (3 ml) was refluxed for 24 h. After evaporation of the solvent and fractional distillation 1-diethylamino-3-trimethylstannoxypropane (**35**) was obtained (1.0 g, 35%), b.p. 43—45 °C at 0.75 mmHg.

2-Methyloxetane (**20**). 2-Methyloxetane (0.62 g, 10 mmol) and TMSnDEA (2.32 g, 10 mmol) were poured into a tube which was sealed and kept at 100 °C for 2 days. The reaction mixture was then fractionated under vacuum to give 1-diethylamino-3-trimethylstannoxypropane (**36**) (1.03 g, 31%), b.p. 68—70 °C at 0.60 mmHg.

General Procedure for the Demetallation of the Siloxy Adducts.—The siloxy adduct (0.5 g) was dissolved in dry Et_2O (5 ml), the solution was cooled to 0 °C, and then gaseous HCl was passed through. Immediately a white-yellow precipitate formed; the passage of HCl was maintained for 5—15 min, then the ethereal layer was decanted, and the solid was dissolved in CH_2Cl_2 (5—10 ml) and washed three times with 10% $NaHCO_3$ solution and twice with water. The organic layer was dried (Na_2SO_4) and, after evaporation of the solvent and vacuum distillation, the corresponding amino alcohols (**9**), (**10**), (**12**), and (**25**)—(**27**) were obtained in yields of 79—89%.

1,1-*Diethylamino*-1-*phenylpropan*-2-*ol* (**11**). Following the general procedure, compound (**11**) (0.30 g, 79%) was obtained by fractional distillation, b.p. 198—200 °C at 36 mmHg; δ 1.1 (6 H, m, $EtCH_3$), 1.14 (3 H, d, *J* 6 Hz, CH_3CO), 2.2—2.9 (4 H, m, $EtCH_2$), 3.2 (1 H, br OH), 3.60 (1 H, d, *J* 7 Hz, NCH), 4.4 (1 H, m, OCH), and 7.4 (5 H, m, ArH); *m/z* 192 ($M^+ - 15$), 162 (base) (Found: C, 75.45; H, 10.1. $C_{13}H_{21}NO$ requires C, 75.36; H 10.14%).

Destannylation of the stannyl adducts (**34**)—(**36**) was performed with the malonic acid system previously described.[3]

Acknowledgements

This work has been carried out with the financial support of Progetto Finalizzato Chimica Fine e Secondaria of C.N.R., Rome,

References

1 J. G. Buchanan and H. R. Soble, 'Selective Organic Transformations', ed. B. S. Thyagarajan, John Wiley and Sons, New York, 1972, vol. 2, p. 1.
2 M. Fiorenza, A. Ricci, M. Taddei, D. Tassi, and G. Seconi, *Synthesis*, 1983, 640.
3 M. Taddei, A. Papini, M. Fiorenza, A. Ricci, and G. Seconi, *Tetrahedron Lett.*, 1983, **24**, 2311.
4 A. Ricci, M. N. Romanelli, M. Taddei, G. Seconi, and A. Shanzer, *Synthesis*, 1983, 319.
5 R. A. W. Johnstone, 'Mass Spectrometry for Organic Chemists,' Cambridge University Press, Cambridge, 1972, p. 72.
6 J. C. Mullis and W. P. Weber, *J. Org. Chem.*, 1982, **47**, 2873.
7 L. E. Overman and L. A. Flippin, *Tetrahedron Lett.*, 1981, **22**, 195.
8 K. Itoh, S. Sakay, and Y. Ishii, *J. Org. Chem.*, 1966, **31**, 3948.
9 K. Jones and M. F. Lappert, *J. Chem. Soc.*, 1965, 1944.
10 S. D. Ross, *J. Am. Chem. Soc.*, 1947, **69**, 2982.
11 'Beilsteins Handbuch der Organischen Chemie,' IV, **13**, 709.
12 F. L. Pyman, *J. Chem. Soc.*, 1917, **111**, 170.
13 R. Munch, G. T. Thannauser, and D. L. Cottle, *J. Am. Chem. Soc.*, 1946, **68**, 1297.
14 R. C. Elderfield *et al.*, *J. Am. Chem. Soc.*, 1946, **68**, 1516.
15 Y. Kasuya and K. Fujie, *Yakugaku Zasshi*, 1958, **78**, 551.

Received 16*th January* 1984; *Paper* 4/077