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RING OPENING REACTIONS OF THIIRANES WITH GROUP IV B ORGANOMETALLICS: A NEW REGIOSELECTIVE ROUTE TO β-AMINO AND β-CYANIDE THIOLS.

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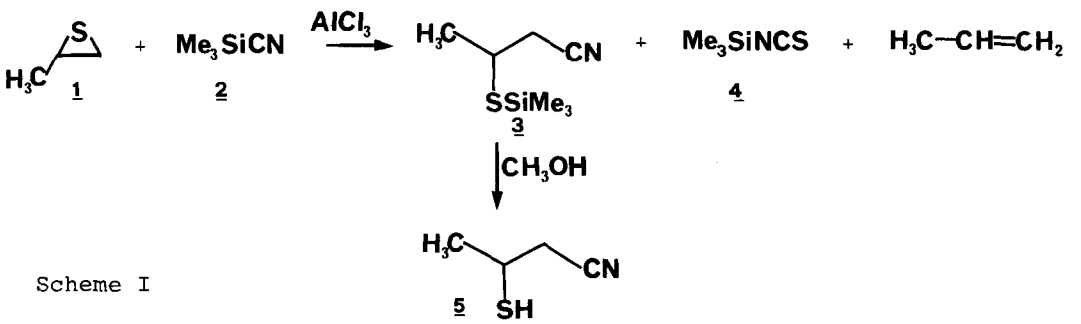
Summary: Regioselective opening of the thiirane ring occurs spontaneously with Group IV B organometallics such as Me_3SnNR_2 and under the catalytic action of $AlCl_3$ with Me_3SiCN,affording difunctional thiols.

Although the reactions of oxiranes with organometallics have been largely developed[1],the corresponding cyclic thioethers have not been the subject of extensive investigations mainly due to the easy desulphuration of these heterocyclic rings with organometallics[2].

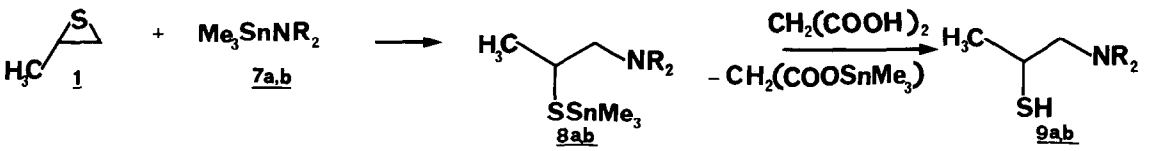
In this paper we describe the reaction between thiiranes and Group IV B organometallic derivatives as a new regioselective route to β-difunctional mercapto compounds.

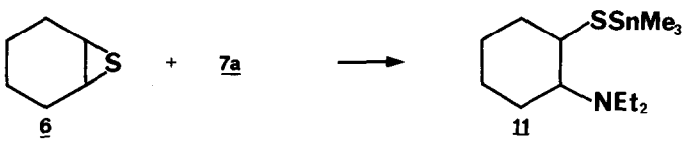
In fact,treating 2-methylthiirane(1)with Me_3SiCN(2) in the presence of $AlCl_3$ as Lewis acid catalyst,a regioselective opening of the heterocyclic ring occurred, giving rise to 2-trimethylsilylthiopropionitrile(3)in satisfactory yields(Scheme I).Trimethylsilylisothiocyanate(4) was also obtained together with propylene fror

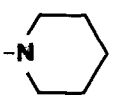


Scheme I

desulphuration of the cyclic thioether and was easily separated from 3 by fractional distillation.Preparation of 3 and 4 is illustrated by the following procedure : 2.96 g(39.9 mmol) of 1 and 3.96 g(39.9 mmol)of 2 were refluxed with 10% molar equivalent of $AlCl_3$,in dry CH_2Cl_2(6 ml) for 16 hours[3];after evaporation of the solvent,compounds 3 and 4 were separated by fractional distillation and fully characterized by GC/mass and ^1H NMR analyses : 3 b.p. 84-85°C/1.5 mmHg,42% yield ^1H NMR($CDCl_3$/TMS) δ 0.50(s.9H),1.51(d.3H,J=7Hz),2.70(d.2H,J=6Hz),3.30ppm(m.1H); IR (liquid film) ν_{CN} 2240 cm^{-1};mass spectrum m/e 173(M^+),73(base);4 b.p.78-79°C/ 1.5 mmHg,IR(liquid film) ν_{NCS} 2080 cm^{-1},mass spectrum m/e 131(M^+),116(base)[4]. By treatment of 3 with CH_3OH in boiling CCl_4,2-mercaptopropionitrile(5) was obtained in quantitative yield : 5 ^1H NMR δ 1.45(d.3H,J=7Hz),1.95(d.1H J=7Hz,-SH), 2.68(d.2H,J=6Hz),3.28ppm(m.1H);IR(liquid film) ν_{SH} 2550,ν_{CN} 2250 cm^{-1}.These data indicated that the only reaction product was the secondary SH isomer,the isomeric purity being confirmed by an accurate GC analysis.Use of 7-thiabicyclo [4, 1.0] heptane(6),under the same reaction conditions,gave no satisfactory results due to the prevailing thiirane polymerisation induced by the catalyst.
High yields in compound 3 were strictly correlated with the use of $AlCl_3$ as Lewis acid catalyst but decreased dramatically with $ZnBr_2$ or $ZnCl_2$;no traces of insertion products were observed with $TiCl_4$ in which case a rapid polymerisation of 1 took place[5],affording unreacted Me_3SiCN.A similar behaviour was observed in the reaction of the thiirane ring with different organosilicon compounds such as Me_3SiX,X=Br,I,NEt_2,SPh,N_3,both with $AlCl_3$ and other Lewis acid catalysts. Although the regioselective ring opening of 1 failed with $AlCl_3$and aminosilane, the insertion of an amino group was possible using Me_3SnNR_2 without catalyst (Scheme II).





a): $-NR_2 = -N(C_2H_5)_2$; b): $-NR_2 =$ 

Scheme II

In fact by treating 1.50 g(20.2 mmol) of 1 with the equimolar amount of 7 in boiling dry CH_2Cl_2 under nitrogen for 24 hours,we obtained,after evaporation of the solvent and vacuum distillation,compounds 8 in good yields:8a b.p.88-89°C/ 0.30 mmHg,78% yield,^{1}H NMR ($CDCl_3$/TMS) δ 0.36(s.9H),1.11(t.6H),1.45(d.3H,J=6Hz), 2.55(m.6H),2.95(m.1H);8b b.p. 97-98°C/0.30 mmHg,75% yield,^{1}H NMR($CDCl_3$/TMS) δ 0.25(s.9H),1.30(d.3H,J=7Hz),1.45(m.6H),2.41(m.6H),3.19(m.1H).[6]

In the absence of the Lewis acid catalyst also the ring opening of 6 by 7a occurred,giving rise to 1-diethylamino,2-trimethylstannylthiocyclohexane(11a)which was obtained after 24 hours in boiling dry CH_2Cl_2 and subsequent fractional distillation :11a b.p. 56-57°C/0.15 mmHg,^{1}H NMR signals were in good agreement with the forecasted structure related to a mixture of diastereoisomers.

Unfortunately the lower reactivity of organotin derivatives containing Sn-O and $Sn-N_3$ bonds did not allow a ready insertion with 1 or 6,even with the aid of the catalyst.

The interest in the preparation of the corresponding aminothiols stimulated us to provide an efficient method for destannylation of the thiostannyl derivatives. The best results were obtained by warming a mixture of one equivalent of malonic acid and one equivalent of 8 at 150°C under vacuum(1.5 mmHg),and trapping the volatile aminothiols produced by the electrophilic addition of malonic acid on the tin-sulphur bond.Compounds 9a and 9b,obtained in an overall yield of 71% and 68% respectively and purified by fractional distillation,showed boiling points and spectral properties in good agreement with literature data[2,7].

The reactions of thiiranes with Group IV B organometallic compounds provide a synthetically attractive new regioselective method of functionalising these heterocyclic rings,giving rise to difunctional compounds.Attempts to extend this reaction to other cyclic thioethers and to other silicon and tin derivatives are currently underway .

REFERENCES AND NOTES

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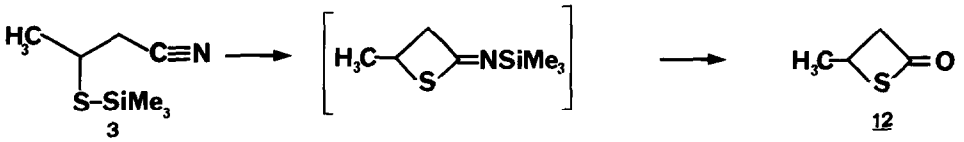
2. For a complete review on the argument see : M.Sander *Chem.Rev.*66,297,(1966). To our knowledge the only reports concerning reactions of thiiranes with or-

ganometallics refer to desulphuration with organo-lithium or Grignard reagents . F.G.Bordwell,H.M.Andersen and B.M.Pitt,*J.Am.Chem.Soc.* 76,1082,(1954). M.Morton and R.F.Kammerec,*J.Am.Chem.Soc.* 92,3217,(1970).

3. IR and GC mass analyses showed traces of 4-methylthiethanone(12)in the crude reaction mixture probably coming from a rearrangement of 3 and subsequent de silylation by air moisture.



All the attempts to increase the yields of 12 gave unsatisfactory results. 12 : IR ν_{CO} 1800 cm^{-1},mass spectrum m/e 102(M^+),91(base).

4. Compound 4 had the same spectral properties as the commercial sample of trimethylsilylisothiocyanate produced by Fluka AG chemicals.
5. S.Boileau and P.Sigwald,*Compt.Rend.* 252,882,(1961).
6. The structure and the isomeric purity of 8a and 8b were also confirmed by the ^{13}C NMR analysis : 8a($CDCl_3$/TMS) δ 4.74,11.48,24.20,35.73,47.31,63.70; 8b ($CDCl_3$/TMS) δ 4.14,25.50,27.60,47.80,49.31,64.20 .
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