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Preliminary communication

FLUORIDE ION-INDUCED RING ENLARGEMENT OF SILICON TRICYCLES

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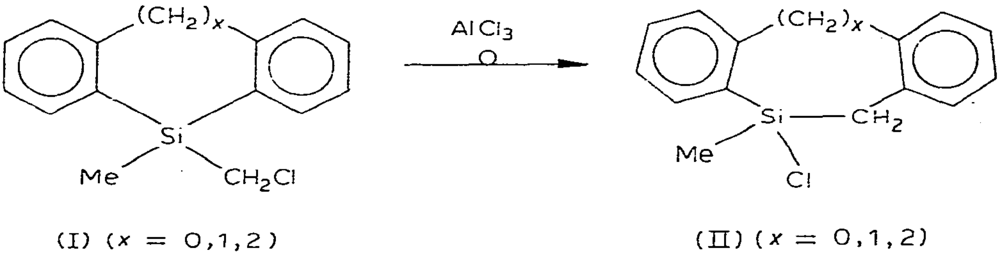
Summary

Ring enlargement of tricyclic silicon heterocycles which contain an exocyclic chloromethyl group on silicon occurs in the presence of KF in refluxing CH_3CN.

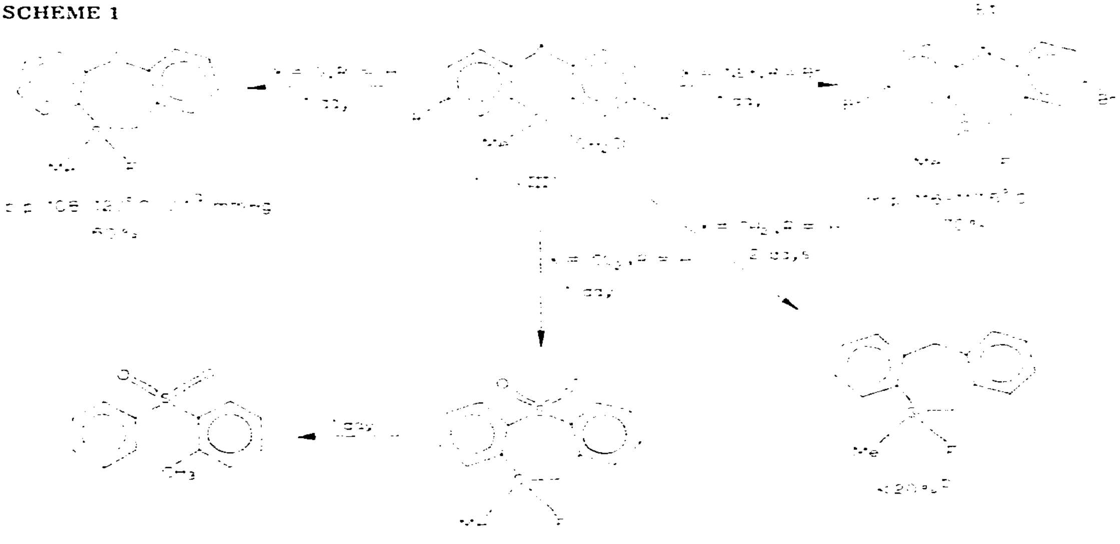
We have reported previously an example of the utility of an aluminum chloride-catalyzed rearrangement reaction for the formation of silicon heterocycles which contain an unsymmetrical framework (eq. 1) [1]. Although the chlorides, II, were not isolated, products of the reaction of II with MeONa, H_2O or $LiAlH_4$ were prepared. There are two inherent disadvantages of this process. Replacement of methylene group in I by a heteroatom with a lone pair results in the formation of a complex on addition of $AlCl_3$ and no ring enlargement. If siloxane impurities are present in I (a normal consequence of the method of preparation) no rearrangement takes place. Both disadvantages would be eliminated if the transformation depicted in Eqn. 1 could be initiated by an anion. Such a reaction could involve attack at silicon prior to rearrangement, in which case fluoride ion would be the anion of choice.



(1)

We wish to report here the preliminary results of a study of the reaction of KF with tricyclic silicon heterocycles in refluxing acetonitrile (Scheme 1). The

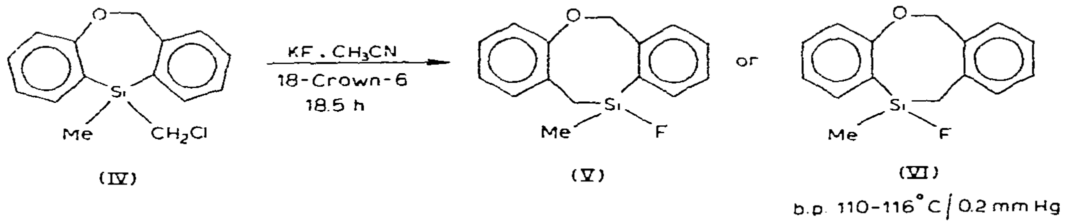
SCHEME 1



a. Kugelrohr distillation b. Mixed with starting material

preparations of the starting ring systems, III, have been described previously [2—5]. The ring enlargement occurs with KF (technical grade dried at 110°C for 48 h prior to use) or KF • HF (ratio of F^-/III = 2/1) and normally takes 24 to 48 h. The presence of 18-crown-6 reduces the time period but does not change the % yield. No rearrangement of III is observed in refluxing CH_3CN over a 7 day period in the absence of F^-. Products were isolated after hydrolysis and distillation of the residue. The NMR spectral data are all similar and in addition to the aromatic protons exhibit a broad Si-CH_2-Ar multiplet in the ^1H NMR spectrum between 2.0 and 3.0 ppm and a doublet Si-Me between 0.3 and 0.4 (*J*(HCSiF) 7.2 Hz). Mass spectral data are consistent with the indicated products as is the chemical analysis obtained for the products from III (X = O, R = H; X = NEt, R = Br). The reaction of the sulfone, III (X = SO_2, R = H) was examined under the same conditions at both a 2/1 and 1/1 ratio of KF/III. After 24 h, starting material and two products which included the expected ring-expansion product and a ring cleavage product were evident in the NMR spectrum of the reaction mixture. After 48 h, only a trace of ring expanded product was present and the ring cleavage product, phenyl(o-tolyl)sulfone, was isolated in approximately 90% yield.

A single example of an expansion of a seven- to an eight-membered ring was examined (eq. 2) [6,7]. The yields are lower for the same time periods used for expansion of III and, although only one ring expanded product appears to have been obtained, it has not yet been determined whether it is V or its isomer VI. The distilled reaction product is contaminated with ring cleavage products but only one FSiMe doublet is observed at 0.3—0.23 ppm (TMS). Reduction of V with $LiAlH_4$ gave the corresponding silane with only one Si-Me doublet at 0.50—0.46 ppm (TMS).



(2)

A substitution of KOAc for KF resulted in conversion of the chloromethyl group of III (X = O, R = H) to CH_2OAc (substitution at carbon and no observable ring rearrangement products). When KF · $2H_2O$ was employed instead of dried technical KF for expansion of III (X = O, R = H), the reaction time was slower but the same yield of ring - expanded product was realized.

The F^- rearrangement with prior attack at silicon has been suggested as an explanation for conversion of Me_3SiCH_2I to Me_2EtSiF with KF/DMF [6] a reaction which does not occur in CH_3CN. A thermal rearrangement of $Ph_3SiCHFPh$ to $Ph_2SiFCHPh_2$ has also been reported (160°C) [7] and treatment of Me_3SiCH_2OH with the Yarovenko reagent, $HClC(F)CF_2NEt_2$, gave 12% of rearranged product, Me_2EtSiF, in addition to the normal substitution product [8].

Although the results described in Scheme 1 are consistent with a rearrangement induced by attack at a silicon center, the alternate possibility of substitution at carbon prior to rearrangement cannot yet be excluded. A study of anion-induced rearrangement of both cyclic and acyclic halomethylsilanes is in progress.

Acknowledgement

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