CHEMISTRY LETTERS, pp. 235-236, 1987.

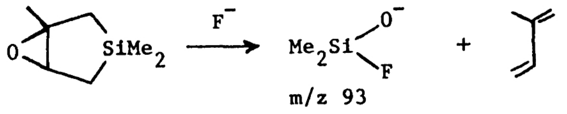
Gas Phase Negative Ion Chemistry of 6-Oxa-3-sila- and Germabicyclo[3.1.0]hexanes

Robert DAMRAUER,* William P. WEBER,† and Georges MANUEL††
Department of Chemistry, University of Colorado at Denver,
Denver, Colorado 80202, U.S.A.
† Loker Hydrocarbon Research Institute and Department of Chemistry,
University of Southern California, Los Angeles, California 90089-1661, U.S.A.
†† Laboratoire des Organometalliqùes, Université Paul-Sabatier
31062 Toulouse, Cedex, France

Ion-molecule reactions between fluoride and 1,3,3-trimethyl-6-oxa-3-silabicyclo[3.1.0]hexane, 2,7-dimethyl-2,3:7,8-diepoxy-5-spiro[4.4]nonane, and 3,3-dimethyl-6-oxa-3-germabicyclo[3.1.0]-hexane are reported. Attack by fluoride at either silicon or germanium results in loss of either isoprene or butadiene, respectively. An analogous reaction with amide ion is reported.

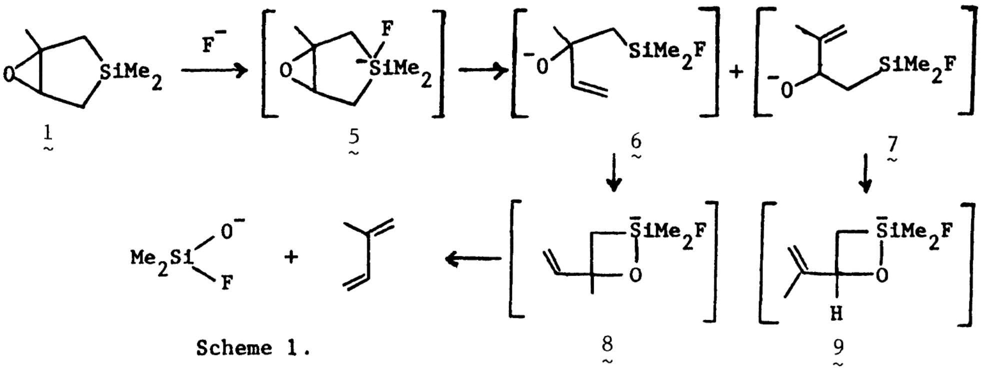
In recent flowing afterglow (FA) studies, we found that 1,3,3-trimethyl-6-oxa-3-silabicyclo[3.1.0]hexane (1) undergoes some remarkable ambient temperature negative ion chemistry.[1)] This, as well as our studies of 2,7-dimethyl-2,3:7,8-diepoxy-5-spiro[4.4]nonane (2), and 3,3-dimethyl-6-oxa-3-germabicyclo[3.1.0]-hexane (3), is reported here.

Fluoride ion, generated from NF_3 in the FA, reacts with 1 to give Me_2SiFO^- (4) under a variety of conditions (Eq. 1). Although this complicated reaction is unprecedented, related examples in solution have been found.[2)] Since the ionic product has silicon bound to fluorine, we assume that this gas phase reaction is initiated by nucleophilic F^- attack at silicon. Scheme 1 outlines



(1)

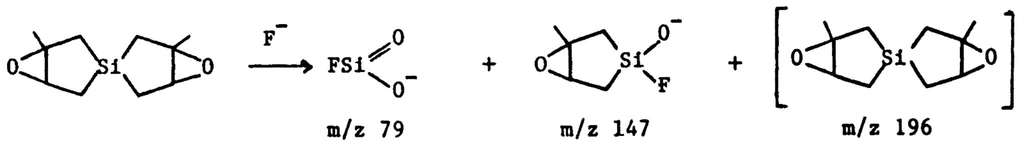
4



Scheme 1.

several possible pathways for this reaction. Indeed, although it is possible that attack at silicon followed by concerted formation of 4 and loss of isoprene is occurring, stepwise pathways which involve the intermediacy of 5-9, are possible. Only ion 4 is observed. The nature of these FA experiments, in which only anions are detected, makes the identification of neutral products difficult and limits mechanistic information.

Both 2 and 3 react similarly. The spiro compound, 2, gives three identifiable ions: m/z = 79 (minor), 147 (major), and 196 (major) (Eq. 2). Ion 10

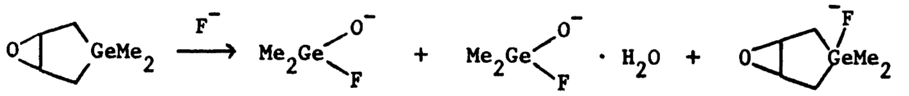


(2)

2 10 11

is analogous to the product obtained from 1. A structure of $FSi{=}O(O^-)$ for the m/z = 79 ion is reasonable, as it may arise from the decomposition of 10. Ion 11 appears to result from electron attachment to 2. While excess electrons are common in a FA plasma NF_3, it is unusual to observe electron attachment products.

The germanium compound 3 also results with F^- giving Me_2GeFO^- (12), and small amounts of $Me_2GeFO^- \cdot H_2O$ (13) and the fluoride adduct (14) (Eq. 3). Ion 12,



(3)

3 12 13 14

is analogous to 4. We are uncertain about the origin of ion 13. It may form from small quantities of water in the flowtube. We have formulated ion 14 as a pentacoordinate germanium species. In a variety of silicon compounds studied in the FA, F^- reacts to give pentacoordinate siliconates.[1,3)]

The reactivity of 1 and 3 with H_2N^-, N_3^-, and HS^- have also been studied. Although neither reacts with N_3^- or HS^-, H_2N^- does with both. Two identifiable ions are observed for 1. One corresponds to its M-1 ion, the other to $Me_2SiNH_2O^-$. Several other ions are observed, but these have not yet been identified. Amide ion also reacts with 3, to give an M-1 ion and $Me_2GeNH_2O^-$.

R.D. thanks the National Science Foundation for support CHE-83-13826 and CHE-85-19503 and C.H. DePuy for the use of the FA equipment and his efforts in making our collaboration fruitful. W.P.W. thanks the Air Force Office of Scientific Research, Grant 86-0042.

References

1) For a review of FA silicon studies see: C.H. DePuy, R. Damrauer, J.H. Bowie, and J.C. Shelton, Gas Phase Organosilicon Chemistry, Acc. Chem. Res., submitted for publication, 1986.

2) A. Bacereido, C.D. Juengst, G. Manuel, and W.P. Weber, Chem. Lett., following letter.

3) S.A. Sullivan, C.H. DePuy, and R. Damrauer, J. Am. Chem. Soc., 103, 480 (1981); R. Damrauer and C.H. DePuy, Organometallics, 3, 362 (1984); R. Damrauer, C.H. DePuy, and V.M. Bierbaum, ibid., 1, 1553 (1982).

(Received October 18, 1986)