

Preliminary communication

Reactions of functionally substituted 1,3,5,7-tetrasiladamantanes with electrophilic reagents

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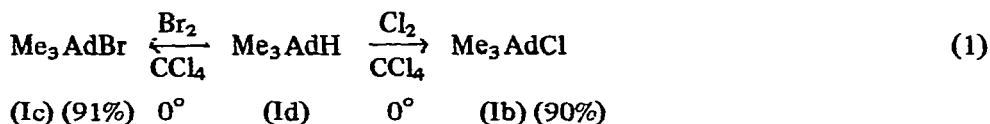
SUMMARY

The reactivity pattern of 3,5,7-trimethyl-1,3,5,7-tetrasiladamantyl hydride and 1-methoxy-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane with electrophilic reagents are discussed with respect to mechanistic implications.

The reactivity of the tetrasiladamantyl chlorides (Ia), AdCl_4 , and (Ib), Me_3AdCl , toward nucleophilic reagents has been investigated to some extent¹⁻³. The relatively rigid ground state geometry of these compounds renders them "reluctantly reactive"² to many, but not all³ nucleophilic reagents. We have recently shown that this relatively rigid geometry does not hinder the formation and reactions of the adamantyl silicon radical from (Id), Me_3AdH ⁴. We now wish to report the first reactions of tetrasiladamantanes with strong electrophilic reagents. These reactions reveal new facets of the reactivity pattern of this interesting cage system.

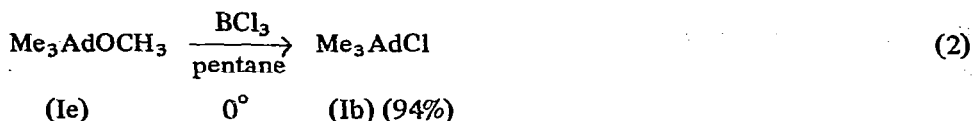
The tetrasiladamantane system was prepared by the method of Frye⁵. All the compounds reported in this paper were characterized by IR, NMR and mass spectroscopy, and elemental analysis.

The tetrasiladamantyl hydride (Id) reacts with Cl_2 or Br_2 in CCl_4 to give (Ib) and (Ic) respectively in high yield and purity (Eqn. 1). Both reactions were instantaneous and exothermic under highly subdued light. The reaction of BCl_3 in pentane with (Ie) also



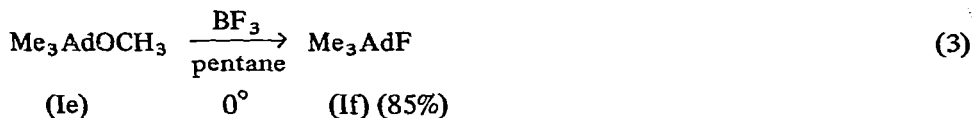
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gave (Ib) in an instantaneous reaction (Eqn. 2). Both of these reactions are known to proceed by similar mechanisms which lead to retention of configuration at silicon when



carried out on optically active acyclic organosilicon compounds^{6,7}. Clearly, such mechanisms are not hindered by the unique geometry of the tetrasiladamantane system.

A dramatic change occurs when BF_3 is reacted with (Ie) in pentane (Eqn. 3) under the same conditions used for BCl_3 . The reaction is now very slow (50% after 30 h) and



required approximately 6 days to go to completion as indicated by periodic GLC analysis. This result is consistent with the results obtained with optically active acyclic organosilicon methoxides which showed that BF_3 , in contrast to BCl_3 , reacts by a mechanism which leads to inversion of configuration at silicon⁷. Such a mechanism is impossible for the tetrasiladamantane system. Thus the reaction is apparently forced to follow a mechanism less favorable to the nature of the reagent and is therefore very slow.

Additional work in this area is presently under way as part of our continuing study of the reactivity at adamantyl silicon.

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