

Preliminary communication

Facile reactions of functionally substituted 1,3,5,7-tetrasiladamantanes with nucleophilic reagents

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SUMMARY

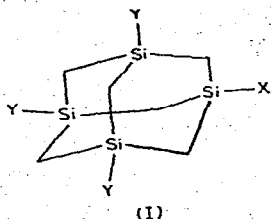
The first facile nucleophilic displacement reactions of functionally-substituted tetrasiladamantanes are reported and are in dramatic contrast to the previously reported lack of reactivity of this system toward nucleophilic reagents.

In 1961 Smith and Clark¹ reported that the tetrasiladamantyl chloride (Ia), AdCl_4 , was inert to hydrolysis and extremely resistant to methylation with CH_3MgCl . Recently Frye and Klosowski² reported similar observations for the tetrasiladamantyl chloride (Ib), Me_3AdCl . This material was inert to hydrolysis in moist acetone containing Et_3N for a period of one month and was very sluggish in its reduction with LiAlH_4 . Vigorous forcing conditions were ultimately required to achieve these transformations. This highly unusual lack of reactivity toward nucleophiles such as water and ethereal LiAlH_4 is believed to be due to the relatively rigid and strain free ground state geometry^{3,4}.

We now wish to communicate recent results which are in sharp and dramatic contrast to the previously reported lack of reactivity at silicon centers in the tetrasiladamantane system. These results clearly show that this system is not universally unreactive toward nucleophilic reagents in spite of its unique ground state geometry.

Most of the work was carried out on 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ib), Me_3AdCl . All tetrasiladamantane derivatives reported in this paper were characterized by IR, NMR, mass spectroscopy, and elemental analysis. The progress of the reactions was following as a function of time by GLC and all the reported yields are isolated yields. The results are summarized in Table 1.

In addition to the results shown in Table 1, it was found that (Ic), $\text{Me}_3\text{AdOCH}_3$, was readily reduced by diisobutylaluminum hydride, $(i\text{-Bu})_2\text{AlH}$, in ether (eqn. 1). This



- a; Y = X = Cl
 b; Y = CH₃, X = Cl
 c; Y = CH₃, X = OCH₃
 d; Y = CH₃, X = H
 e; Y = CH₃, X = OH
 f; Y = CH₃, X = F

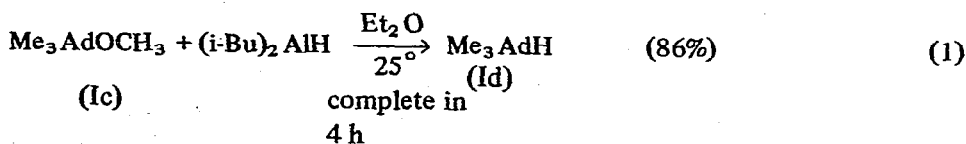
TABLE 1

NUCLEOPHILIC SUBSTITUTION REACTIONS OF Me₃AdCl

Reaction No.	Reagent	Solvent	Reaction temperature (°C)	Reaction time	Product	Yield (%)
1	NaOCH ₃	CH ₃ OH	25	<15 min ^a	Me ₃ AdOCH ₃	86
2	PhCH ₂ N(CH ₃) ₃ O ⁻ H	CH ₃ OH	25	<15 min ^a	Me ₃ AdOCH ₃ ^b	92
3	CH ₃ OH	CH ₃ OH	25	24 h	^c	—
4	<i>o</i> -C ₆ H ₁₁ NH ₃ ⁺ F ⁻	CH ₃ OH	25	1.5 h	Me ₃ AdF	90
5	<i>o</i> -C ₆ H ₁₁ NH ₃ ⁺ F ⁻	CHCl ₃	25	12 h	Me ₃ AdF	89
6	CH ₃ Li	Et ₂ O/TMEDA ^d	25	30 min	Me ₃ AdCH ₃	70

^a The reaction was about 90% complete 5 min after mixing by GLC analysis. ^b Me₃AdOCH₃ was virtually the only product. A small peak, <1% of the total, was detected by GLC in addition to the Me₃AdOCH₃ peak. This peak was presumably the silanol, Me₃AdOH. ^c No reaction was detected by GLC. The starting material was recovered and identified by IR and m.p. ^d *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) was present in equimolar amounts relative to CH₃Li.

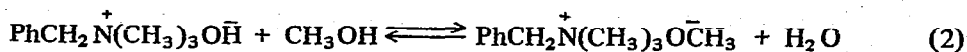
result is made even more dramatic by the fact that we have found that the acyclic analog,



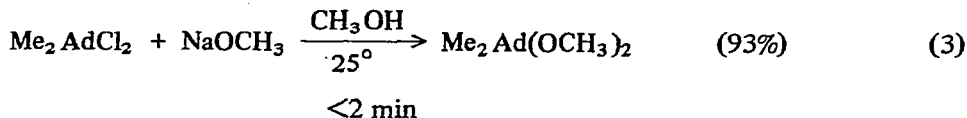
(Me₃SiCH₂)₃SiOCH₃, is reduced more slowly than Me₃AdOCH₃ by a factor of at least 100. Thus, under certain conditions, the tetrasilaadamantyl system actually shows enhanced reactivity relative to analogous non-rigid systems.

Reactions 1–3 show that while Me₃AdCl is inert to CH₃OH alone it does undergo facile methanolysis with CH₃O⁻ in methanol solution. In the case of reaction 2 an equilib-

rium between the ammonium hydroxide and the ammonium methoxide in methanol solution must exist (eq. 2) with the rate of formation of $\text{Me}_3\text{AdOCH}_3$ greatly exceeding the rate of formation of (Ie), Me_3AdOH , under these conditions. It is also interesting to note that the



difunctional derivative 1,3-dichloro-5,7-dimethyl-1,3,5,7-tetrasiladamantane (Me_2AdCl_2) is even more reactive toward NaOCH_3 in CH_3OH than Me_3AdCl under similar conditions (eq. 3). Both chlorines are replaced in less than two minutes after mixing as indicated by



GLC analysis of the reaction mixture. This interesting observation is currently being investigated in greater detail.

Reaction 4 and 5, though less dramatic than the methanolysis experiments, are further examples of facile nucleophilic displacements at a tetrasiladamantyl silicon center. Evidently an increase in bulk solvent polarity leads to an increase in the rate of formation of (If), Me_3AdF , as indicated by the shorter reaction time in CH_3OH solution as compared to CHCl_3 solution.

Reaction 6 shows that Me_3AdCl will also undergo a reasonably facile coupling reaction with an activated organometallic reagent. The reaction of Me_3AdCl with CH_3Li in the absence of TMEDA is very slow.

Clearly, facile mechanistic pathways for nucleophilic substitution are available to this unique system in spite of its relatively rigid and strain free ground state geometry. An $S_{\text{N}}i\text{-Si}$ mechanism⁵ is undoubtedly operating for the reaction shown in eq. 1 since it is known that this mechanism is favored for $(i\text{-Bu})_2\text{AlH}$ reductions of alkoxy silanes⁶. However, a different mechanism is probably operating for reaction 2 since one would not expect a strong interaction between the $\text{PhCH}_2\overset{+}{\text{N}}(\text{CH}_3)_3$ cation and the leaving chloride. An $S_{\text{N}}2\text{-Si}$ (retention) mechanism⁵ is more likely for this reaction. The remaining reactions reported in this paper probably follow this mechanism as well. However, other mechanisms are still possible and a more detailed study of this system and appropriate model systems is presently under way in order to obtain a better understanding of the mechanisms involved.

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