Journal of Organometallic Chemistry, 84 (1975) 297—304
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REACTIVITY STUDIES OF BRIDGEHEAD ORGANOSILICON COMPOUNDS WITH ELECTROPHILIC AND RADICAL CHLORINATING REAGENTS

G.D. HOMER and L.H. SOMMER *

Department of Chemistry, University of California, Davis, California 95616 (U.S.A.)

(Received June 21st, 1974)

Summary

The relative reactivity toward electrophilic and radical chlorination of 3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane (Ia, Me_3AdH), 1-silabicyclo[2.2.1]-heptane (IIa), 1-silabicyclo[2.2.2]octane (IIIa) and analogous model systems was determined. For both reactions, the angle-strained bridgehead silanes IIa and IIIa are less reactive than Me_3AdH which is relatively strain free. The results for radical chlorination are interpreted primarily in terms of differences in ground state geometry. The results for electrophilic chlorination appear to be due primarily to polar effects with ground state geometry also playing an important role. It is known that polar effects are far more significant for electrophilic chlorination than for radical chlorination at silicon centers.

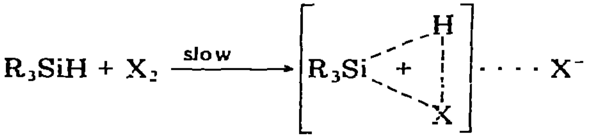
Introduction

Bridgehead compounds offer a unique situation in the study of reaction mechanisms. Unlike non-cyclic systems, bridgehead systems due to their relatively rigid geometry, are not free to assume any configuration in the transition state or intermediate in order to best satisfy the overall conditions of a given reaction. They are, in fact, constrained to a transition state or intermediate geometry which has to be similar to the ground state geometry. Therefore, if the transition state structural requirements for a given reaction are not well satisfied by this geometry the reaction will be correspondingly retarded. Thus the study of bridgehead compounds is especially capable of leading to a more firmly based understanding of transition state structure.

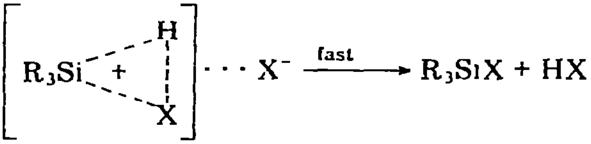
The relative reactivities of bridgehead organosilicon compounds toward nucleophilic displacement at silicon have been studied in some detail [1]. The mechanisms involved in nucleophilic displacement at bridgehead silicon are more clearly understood as a result of these studies.

Considerably less is known about the relative reactivities and the mechanisms involved for bridgehead organosilicon compounds in reactions that involve electrophilic attack on silicon. The same is true for reactions that proceed via silicon-centered radicals.

Comprehensive studies [2, 3] of the halogenation of R_3SiH compounds with X_2 in CCl_4 have established several important points: (1) the reaction follows a second-order rate law, rate = $k_2[R_3SiH][X_2]$; (2) the reaction is highly stereospecific and proceeds with retention of configuration at silicon; (3) the reaction involves electrophilic attack of X^+ on silicon; and (4) polar effects are large with electron-withdrawing groups retarding the rate as indicated by $\rho^* = -4.2$. The mechanism proposed for this reaction is shown in eqns. 1 and 2.



(1)



(2)

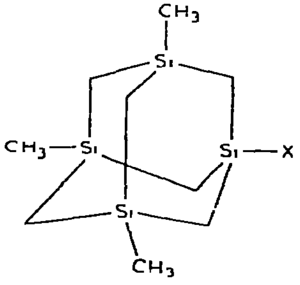
Thus this reaction is an excellent model for electrophilic reactions at silicon. Furthermore, kinetic studies [2, 3] established a relative reactivity order for a wide variety of organosilanes including two bridgehead silanes; 1-silabicyclo[2.2.1]heptane (IIa) and 1-silabicyclo[2.2.2]octane (IIIa). These studies clearly showed that the two bridgehead silanes are less reactive than either cyclic or non-cyclic silanes (see below).

$$\text{Relative rates } \mathrm{PrMe_2SiH} \sim \mathrm{IVa} > \mathrm{IIIa} > \mathrm{IIa} \qquad (3)$$

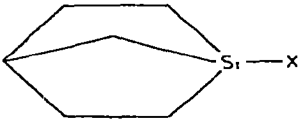
$$1.0 \qquad 1.0 \qquad 0.06 \qquad 10^{-3}$$

Recently it has been shown that 3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane (Ia, Me_3AdH) undergoes facile chlorination with Cl_2 in CCl_4 to give (Ib, Me_3AdCl) in high yield [4]. However, no comparison has been made between this relatively strain free system and the other bridgehead organosilanes.

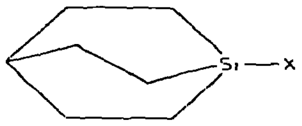
Organosilanes can also undergo chlorination in a radical manner by reaction with alkyl chlorides in the presence of a radical initiator [5]. When the alkyl chloride is CCl_4 and the initiator is benzoyl peroxide the reaction is fast, clean, and uncomplicated by side reactions. The mechanism proposed [6] is shown in eqns. 4-6.



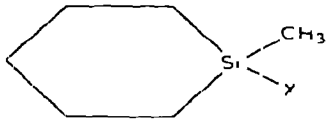
(Ia) X = H
(Ib) X = Cl
(Ic) X = OCH_3



(IIa) X = H
(IIb) X = Cl



(IIIa) X = H
(IIIb) X = Cl



(IVa) X = H
(IVb) X = Cl

$[(CH_3)_3SiCH_2]_3Si—X$

(Va) X = H
(Vb) X = Cl

$$R_3SiH + In \rightarrow R_3Si\cdot + InH \qquad (4)$$

$$R_3Si\cdot + CCl_4 \rightarrow R_3SiCl + \cdot CCl_3 \qquad (5)$$

$$R_3SiH + \cdot CCl_3 \rightarrow R_3Si\cdot + CHCl_3 \qquad (6)$$

A relative rate study for the radical chlorination of silanes with CCl_4 and benzoyl peroxide has been reported [7]. This study showed that the bridgehead silane IIa is slightly less reactive than a silane in which silicon is not a member of a cyclic system.

$$\text{Relative rates} \quad \underset{1.0}{CH_3(C_6H_{11})_2SiH} > \underset{0.33}{\text{IIa}} \qquad (7)$$

It has also been shown that Me_3AdH undergoes radical chlorination much more readily than its non-cyclic analog, tris(trimethylsilylmethyl)silane (Va) [8]. However, no comparison between the bridgehead organosilanes has ever been made for radical chlorinations.

This paper reports the results of a more detailed study of the relative reactivity of the various bridgehead silanes toward both electrophilic and radical chlorination.

Results

The reactions reported in this paper were carried out with five compounds: 3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane (Ia, Me_3AdH), 1-silabicyclo[2.2.1]-heptane (IIa); 1-silabicyclo[2.2.2]octane (IIIa); 1-methyl-1-silacyclohexane (IVa); and tris(trimethylsilylmethyl)silane (Va).

The tetrasilaadamantane system has four bridgehead silicon atoms whose angles should resist distortion from the tetrahedral because of the nature of the ring system which is virtually free from angle strain and from conformational strain as indicated by accurate molecular models [1e,f].

The 1-silabicyclo[2.2.1]heptane system, in contrast to the tetrasilaadamantane system, contains bridgehead silicon in a highly strained geometry. Accurate molecular models of this system indicate that the C—Si—C bond angles probably lie in the 90 to 95° range when the carbon atoms of the ring system maintain tetrahedral geometry [1e].

The angle strain for the 1-silabicyclo[2.2.2]octane system is intermediate between I and II. Accurate molecular models indicate C—Si—C bond angles that are somewhat smaller than tetrahedral when the ring carbon atoms maintain tetrahedral geometry [1e].

The 1-methyl-1-silacyclohexane system simply serves as an analog to II that does not contain angle-strained silicon and is similar in its reactivity to non-cyclic organosilicon compounds.

TABLE 1

RELATIVE RATES FOR ELECTROPHILIC CHLORINATION

Reaction	Substrate	k/k_{Ia}
1	Va	$\sim 10^{2}$ [a]
2	Ia	1.0
3	IVa	0.80 ± 0.10
4	IIa	$\sim 10^{-2}$ [b]

[a] This represents a minimum value for k_{Va}/k_{Ia} (see experimental section).

[b] This represents a maximum value for K_{IIa}/K_{Ia} (see experimental section).

The tris(trimethylsilylmethyl)silane system serves as non-cyclic analog to I that has the characteristic Si—CH_2—Si structure.

All the electrophilic and radical chlorinations were carried out in a competitive manner with Me_3AdH as the standard for comparison. The details of the experiments and the methods used to calculate the relative rate constants are given in the experimental section.

Table 1 shows the results for electrophilic chlorination with Cl_2 in CCl_4.

The data from Table 1 shows that Me_3AdH is comparable in reactivity with 1-methyl-1-silacyclohexane and considerably less reactive than its non-cyclic analog, $(Me_3SiCH_2)_3SiH$. Me_3AdH is also more reactive than the angle strained silane IIa by a factor of at least 10^2 times.

A careful comparison of these data with the data shown in (3) allows the establishment of relative reactivity order for the electrophilic chlorination of the subject silanes: $(Me_3SiCH_2)_3SiH > Me_3AdH \sim PrMe_2SiH \sim IVa > IIIa > IIa$.

For radical chlorination with CCl_4 and benzoyl peroxide, results are given in Table 2.

The results from Table 2 show that Ia is considerably more reactive toward radical chlorination than any of the other silanes. Comparison of reactions 6 and 8 from Table 2 shows that 1-methyl-1-silacyclohexane is about 2.5 times more reactive than 1-silabicyclo[2.2.1]heptane. Comparison of these data with the relative rates shown in (7) indicates that 1-methyl-1-silacyclohexane and the non-cyclic trialkylsilane, $CH_3(C_6H_{11})_2SiH$, have comparable reactivity. The relative reactivity order for radical chlorination is: $Ia > CH_3(C_6H_{11})_2SiH \sim IVa > IIIa > IIa$.

Although this order of relative reactivity has some similarity to the trend for electrophilic chlorination, there are important differences. One major difference is that, in radical chlorination, the spread of relative rates is less than 10^2, whereas in electrophilic chlorination a spread of greater than 10^4 is found.

TABLE 2

RELATIVE RATES FOR RADICAL CHLORINATION

Reaction number	Substrate	k/k_{Ia}
5	Ia	1.00
6	IVa	$(8.1 \pm 0.8) \times 10^{-2}$
7	IIIa	$(5.1 \pm 0.5) \times 10^{-2}$
8	IIa	$(3.2 \pm 0.4) \times 10^{-2}$

Also, Me_3AdH is more reactive in radical chlorination than all the other silanes. Even $(Me_3SiCH_2)_3SiH$, the non-cyclic analog of Me_3AdH, is known to be less reactive than Me_3AdH toward radical chlorination [8]. This is not the case for electrophilic chlorination.

Discussion

The results from Tables 1 and 2 combined with the results from previous work [2,3,7,8] clearly show that the angle strained bridgehead silanes IIa and IIIa are less reactive toward both electrophilic and radical chlorination, than Me_3AdH which is virtually free of strain. It is interesting to note that these relative reactivity patterns are in dramatic contrast to the reactivity pattern observed for nucleophilic substitution at bridgehead silicon [1i] where IIb was found to be much more reactive than Me_3AdCl toward a wide variety of nucleophiles.

The reactivity pattern for nucleophilic substitution at bridgehead silicon was explained in terms of a combination of geometrical and orbital-hybridization factors [1i]. The same factors appear to be critical for electrophilic chlorination as well.

Orbital-hybridization due to angle strain should result in a polar effect which is directionally the same as placing a highly electronegative substituent (such as Cl) on silicon, giving increased reactivity with nucleophiles and decreased reactivity with electrophiles [9]. Since electrophilic chlorination is known to be very sensitive to polar effects ($\rho^+ = -4.2$) [2, 3] the observed reactivity order for Me_3AdH and the two angle strained bridgehead silanes IIa and IIIa is not unexpected.

The fact that $(Me_3SiCH_2)_3SiH$ is by far the most reactive silane toward electrophilic chlorination can also be explained in terms of a polar effect. The Me_3SiCH_2 group is known to be a moderately strong electron donating group [10]. Thus one would expect $(Me_3SiCH_2)_3SiH$ to be highly activated toward electrophiles.

Ground state geometry must also be important since the adamantyl bridgehead silane Me_3AdH is at least 10^2 times less reactive than its non-cyclic analog $(Me_3SiCH_2)_3SiH$ although substituents in both compounds should have similar polar effects. Thus the bridgehead nature of Me_3AdH appears to oppose the favorable polar substituent effect present in both systems.

However, it is important to note that the bridgehead nature of Me_3AdH does not give rise to a slow rate since electrophilic chlorination of Me_3AdH is, in fact, *very fast and exothermic* [4] and competitive with simple non-cyclic and cyclic silanes. Thus a facile mechanistic pathway is also available to Me_3AdH in spite of its relatively rigid cage structure. Based on this data, it is safe to say that the transition state geometry for electrophilic chlorination of Si—H compounds does not require extensive distortion from the normal ground state tetrahedral geometry.

The situation for radical chlorination of Si—H compounds appears to be more clear-cut since polar effects are known to be relatively small for this reaction [6, 7]. The Hammett ρ for this reaction varies from -0.38 to -0.54. It is our opinion that the differences in ground state geometry, which are profound, for the three bridgehead silanes are primarily responsible for the observed relative reactivity pattern for radical chlorination. The data in Table 2 clearly indicates that Me_3AdH, which is locked in tetrahedral geometry about silicon by the relatively rigid cage system, is more reactive toward radical chlorination than all silanes studied. This includes non-cyclic and cyclic silanes as well as the angle strained silanes IIa and IIIa. Me_3AdH is even more reactive than its non-cyclic analog $(Me_3SiCH_2)_3SiH$ [8]. This data tends to indicate that silicon-centered radicals have a strong preference for tetrahedral geometry. This conclusion is in excellent agreement with the results obtained with non-cyclic non-rigid silyl radicals from optically active precursors which show that these radicals prefer to maintain their chirality [11-13]. Dilution experiments [13] for the reaction sequence shown in eqns. 4-6 showed that the silyl radical was slow to invert (racemize) even at relatively high dilution with an inert solvent. Thus the favored geometry for an intermediate silicon-centered radical appears to be very nearly tetrahedral.

Experimental section

Materials

The preparation and characterization of 3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane (Ia), 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane (Ib), 1-silabicyclo[2.2.1]heptane (IIa), 1-chloro-1-silabicyclo[2.2.1]heptane (IIb), tris(trimethylsilylmethyl)silane (Va), and tris(trimethylsilylmethyl)chlorosilane (Vb) is described in detail in a previous paper [1i]. 1-Chloro-1-methyl-1-silacyclohexane (IVb) was available in this laboratory. 1-Methyl-1-silacyclohexane (IVa) was prepared by the $LiAlH_4$ in ethyl ether reduction of IVb and was purified by distillation. B.p. 116-118°C/760 mmHg, n_D^{24} 1.4468 (Lit. [14]: b.p. 118°C/760 mmHg, n_D^{25} 1.4462). 1-Silabicyclo[2.2.2]octane (IIIa) and the corresponding chlorosilane (IIIb) were available in this laboratory. The preparation of IIIa and IIIb has previously been described [1c]. Chlorine was obtained from the Matheson Co. Inc., and used as received. Benzoyl peroxide was obtained from Eastman Organic Chemicals and used as received. Carbon tetrachloride (Mallinckrodt spectrophotometric grade) was used without further purification.

Analytical procedure

All the competition experiments were followed by GLPC using a Hewlett Packard 7620A Gas chromatograph with flame ionization detector and equipped with a 18 ft. × 1/8 in. 3% OV-17 on chromosorb W(HP) 80/100 mesh column. Peak areas were determined by the peak height times peak width at half height method. Flame response factors were determined in the usual manner.

Competition chlorination with Cl_2 in CCl_4; general procedure

Equal molar amounts of Me_3AdH and a competing silane were carefully weighed out and dissolved in CCl_4. A standard solution of Cl_2 in CCl_4 was then added in small portions under subdued light conditions. After an interval of several minutes the reaction mixture was analyzed by GLPC. This process was repeated after each addition of Cl_2 in CCl_4 until the reaction was complete. No side products were observed by GLPC. The relative rate constant for a given competition was calculated from eqn. 8 [15] where P = mole percent of the product and I = initial mole percent of the silane. The reproducibility obtained with this technique was in the order of ±10%.

$$\frac{k_a}{k_b} = \frac{P_a I_b}{P_b I_a} \tag{8}$$

Competition chlorination of Me_3AdH and 1-methyl-1-silacyclohexane with Cl_2 in CCl_4

This reaction was carried out according to the general procedure with 175 mg (0.73 mmol) of Ia and 83 mg (0.73 mmol) of IVb in 5 ml of CCl_4. The relative rate constant, k_{IVa}/k_{Ia}, was calculated to be 0.80 ± 0.10.

Competition chlorination of Me_3AdH and 1-silabicyclo[2.2.1]heptane with Cl_2 in CCl_4

This reaction was carried out according to the general procedure with 350.9 mg (1.45 mmol) of Ia and 161.8 mg (1.45 mmol) of IIa in 10 ml of CCl_4. In this reaction no chlorination of IIa was detected until all the Ia was gone. In order to calculate a maximum value for the relative rate constant, k_{IIa}/k_{Ia}, a sensitivity of ±1.0% was assumed for the flame ionization detector which is more than generous considering the normally high sensitivity associated with these detectors. With this assumption, the maximum value for k_{IIa}/k_{Ia} was calculated to be $\sim 10^{-2}$.

Competition chlorination of Me_3AdH and tris(trimethylsilylmethyl)silane with Cl_2 and CCl_4

This reaction was carried out according to the general procedure with 175 mg (0.73 mmol) of Ia and 212 mg (0.73 mmol) of Va in 5.0 ml of CCl_4. In this reaction no chlorination of Ia was detected until all the Va was gone. In order to calculate a minimum value for the relative rate constant, k_{Va}/k_{Ia}, a sensitivity of ±1.0% was assumed for the flame ionization detector which is more than generous considering the normally high sensitivity associated with these detectors. With this assumption, the minimum value for k_{Va}/k_{Ia} was calculated to be $\sim 10^2$.

Competition chlorination with benzoyl peroxide and CCl_4; general procedure

Equal molar amounts of Me_3AdH and a competing silane were carefully weighed out and dissolved in CCl_4 in a round bottom flask equipped with thermometer, magnetic stirrer, condenser, and maintained under an atmosphere of nitrogen. The reaction mixture was then heated to gentle reflux and a small portion (ten mole percent) of benzoyl peroxide was added to initiate chlorination. The reaction mixture was analyzed periodically by GLPC. No side products were observed by GLPC. The relative rate constant was calculated from the Ingold—Shaw (eqn. 9) ($[SiH]_0$ and $[SiH']_0$ = initial silane concentrations, $[SiH]_f$ and $[SiH']_f$ = final silane concentrations) for competitive chain carrying steps in radical chain reactions [16]. The reproducibility obtained with this technique was in the order of ±10%.

$$\frac{k}{k'} = \frac{\log[\mathrm{SiH}]_0/[\mathrm{SiH}]_f}{\log[\mathrm{SiH'}]_0/[\mathrm{SiH'}]_f} \qquad (9)$$

Competition chlorination of Me_3AdH and 1-methyl-1-silacyclohexane with benzoyl peroxide and CCl_4

This reaction was carried out according to the general procedure with 350.9 mg (1.45 mmol) of Ia and 165 mg (1.45 mmol) of IVa in 10 ml of CCl_4. The reaction was initiated with 30 mg (0.12 mmol) of benzoyl peroxide. The relative rate constant, k_{IVa}/k_{Ia} was calculated to be (8.1 ± 0.8) × 10^{-2}.

Competition chlorination of Me_3AdH and 1-silabicyclo[2.2.2]octane with benzoyl peroxide and CCl_4

This reaction was carried out according to the general procedure with 252 mg (1.04 mmol) of Ia and 131.4 mg (1.04 mmol) of IIIa in 10 ml of CCl_4. The reaction was initiated with 30 mg (0.12 mmol) of benzoyl peroxide. The relative rate constant, k_{IIIa}/k_{Ia} was calculated to be (5.1 ± 0.5) × 10^{-2}.

Competition chlorination of Me_3AdH and 1-silabicyclo[2.2.1]heptane with benzoyl peroxide in CCl_4

This reaction was carried out according to the general procedure with 350.9 mg (1.45 mmol) of Ia and 161.8 mg (1.45 mmol) of IIa in 10 ml of CCl_4. The reaction was initiated with 30 mg (0.12 mmol) of benzoyl peroxide. The relative rate constant, k_{IIa}/k_{Ia} was calculated to be (3.2 ± 0.4) × 10^{-2}.

Acknowledgement

We thank Dow Corning Corporation for vital support including a post-doctoral fellowship for one of us (G.D.H.) We are also very grateful to Dr. C.L. Frye for his generous advice concerning necessary preparations.

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