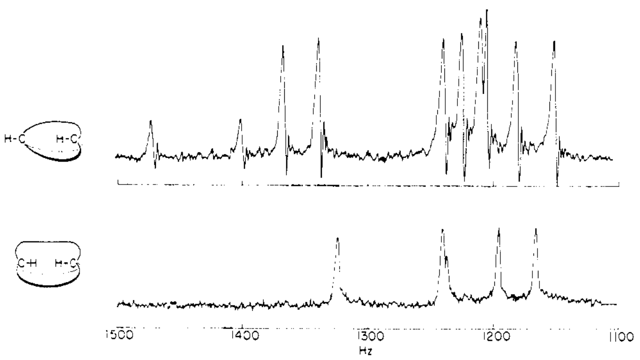

Figure 1. ^{13}C spectra of 2 and 3 in carbon tetrachloride. Chemical shifts are from external methyl iodide at 25.1 MHz.

hydrocarbons by Clemmenson reduction. All new compounds gave satisfactory elemental analyses and molecular weights by mass spectra. The 220-MHz pmr spectra of the bicyclic hydrocarbons did not aid in their structural assignment since the absorptions due to the bridgehead protons are obscured.

The diester *trans*-**8** can give only the out,in hydrocarbon **2**, but the diester *cis*-**8** can lead to both *out,out*-**1** and *in,in*-**3**. In the former case a single hydrocarbon product was observed, the assignment of whose stereochemistry was based on its ^{13}C nmr spectrum which showed ten peaks of appropriate intensity (Figure 1). The assignment of stereochemistry of hydrocarbon derived from the diester *cis*-**8** was based on the following considerations. Theoretical calculations to be published later show that the order of thermodynamic stability of the hydrocarbons is $\mathbf{3} > \mathbf{1} > \mathbf{2}$. If this order is reflected in the cyclization $\mathbf{7} \rightarrow \mathbf{8}$, the single observed product is predicted to be *in,in*-**3**. The ^{13}C spectrum of this product shows five peaks of appropriate intensity but does not readily differentiate between the out,out and in,in atropisomers.

The out,in atropisomer **2** reacts readily with bromine under ionic conditions[6] to give a hexabromide which on catalytic reduction (H_2/Ra–Ni) regenerates the hydrocarbon **2**. On the other hand, the atropisomer derived from *cis*-**8** is inert to bromination under the same conditions. Since tertiary hydrogens in normal environments are rapidly attacked by bromine under these conditions,[6] this suggests that the isomer derived from *cis*-**8** is the in,in atropisomer whose tertiary bridgehead protons must be abnormally shielded from attack by reagents. Experiments to clarify these observations are under way.

[6] R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

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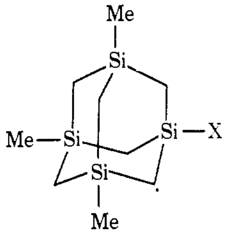
Carborundanes. II. Derivative Chemistry of a Very Reluctantly Reactive Bridgehead Silicon Center

Sir:

In a recent communication[1] a facile synthesis of the 1,3,5,7-tetrasilaadamantane cage system (*i.e.*, the carborundanes) was described. As noted previously,[1,2] nucleophilic displacements at such silicon sites are markedly retarded. We now report some of the more interesting derivative chemistry of this reluctantly reactive tricyclo cage system, including the first example of *a silylamine which is sufficiently robust to be recovered from solution in hydrochloric acid with the Si–N bond still intact!*

We have found it convenient to regard this silmethylene cage as a large nucleus, Ad, with four tetrahedrally disposed valences (*i.e.*, the apical valences of the four bridgehead silicon sites). The work described herein employed the monofunctional cage, Me_3AdX; the



Me_3AdX

various derivatives were isolated, identified, and characterized by appropriate combinations of glc, ir, nmr, and mass spectroscopy (Table I).

Our initial attempt to hydrolyze the chlorosilane, Me_3AdCl, although unsuccessful, does illustrate the solvolytic stability of this material. After 1 month under ambient conditions in a 10% aqueous acetone solution containing Et_3N, this chlorosilane had undergone no detectable reaction. The analogous bromosilane, Me_3AdBr, underwent 75% conversion to the desired silanol, Me_3AdOH, in 9 days under similar conditions. The chloride was subsequently converted to the silanol, but under much more forcing conditions. Thus, Me_3AdCl (1.0 g, 0.0040 mol) was dissolved in moist *tert*-amyl alcohol (9 ml) to which were added $Bu_4N^+Cl^-$ (1.13 g, 0.0040 mol) and KOH (0.184 g, 0.0040 mol). After 30 min at 80°, glc assay indicated almost complete consumption of the starting chlorosilane. Addition of water and extraction with hexane afforded an almost quantitative yield of Me_3AdOH. This same compound was also prepared by heating the silane hydride, Me_3AdH (0.25 g, 8×10^{-4} mol), in dioxane (2 ml) containing water (1.0 g, 0.05 mol) and palladium on carbon[3] (0.5 g of 5% Pd/C) at reflux for 3 days.

The preparation of the silane hydride itself also illustrates the sluggish nature of these displacements. Excess $LiAlH_4$ (0.5 g, 1.3×10^{-2} mol) was added to a mixture of Me_3AdCl and Me_3AdBr (0.5 g total, $\sim 8 \times 10^{-4}$ mol) in ether (100 ml). After 24 hr at reflux, 75 ml of ether was distilled from the system which was then refluxed for an additional 2 hr. Conventional work-up followed by mass spectral assay indicated almost no reduction of the chloride and consumption of only half the bromide. This partially reduced mixture was then refluxed with another 0.5 g of $LiAlH_4$ in ether for 3 days, whereupon the ether was distilled and the residue was baked on a steam bath for 30 min. The residue was then taken up with ether, acetone was cautiously added to decompose the excess $LiAlH_4$,

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[1] C. L. Frye, J. M. Klosowski, and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **92**, 6379 (1970).

[2] A. L. Smith and H. A. Clark, *ibid.*, **83**, 3345 (1961).

[3] G. H. Barnes, Jr., and N. E. Daughenbaugh, *J. Org. Chem.*, **31**, 885 (1966).

Table I. Spectral Data for Monofunctional Tetrasilaadamantanes, Me_3AdX

Compd	Mass spectrometry fragmentation[a]				Nmr[b]			Ir, cm^{-1} (functional group)	Miscellaneous
	P	$P - CH_3$	$P - X$	Other	τ_1	τ_2	Other		
Me_3AdCl	276 (22)	261 (100)	241 (4.1)		9.75	10.22	9.84 ($SiCH_3$)	527 (SiCl)	Mp 147°
Me_3AdOH	258 (6.0)	243 (100)	241 (0.6)		10.005	10.30	9.85 ($SiCH_3$), 2.72 (SiO*H*)	3685 (O–H)	Mp 135°
Me_3AdOCH_2-CH_2NMe_2	329 (3.7)	314 (1.1)	241 (3.2)	58 (100)	10.05	10.29		2780 ($N-CH_3$)	NE[c] 332 (329, theor), bp 165° (6 mm), methiodide mp 246° dec
Me_3AdH	242 (11.6)	227 (100)	241 (5)		(Not run)			~2120 (Si–H)	
Me_3AdNEt_2	313 (10)	298 (90)	241 (100)		10.16	10.32	9.89 ($SiCH_3$), 9.06 (NCH_2-CH_3), 7.20, (NCH_2CH_3)	1203 1177 } ($Si-NEt_2$)	Methiodide decomposes in 170–200° range
Me_3AdMe	256	241 (100)			10.28	10.28	9.91 ($SiCH_3$)	1027 ($SiCH_2Si$) 1248 ($SiCH_3$)	Mp 128°

[a] Only the more significant mass spectrometric data have been shown, *i.e.*, generally the parent ion (P), the ion arising from loss of a methyl group ($P - CH_3$), the ion produced by loss of the functional substituent ($P - X$), and the major ion if it is other than one of these three; relative intensities are shown parenthetically. [b] With few exceptions, only the nmr absorptions of the cage methylene units are shown in this table, τ_1 representing the three sites nearest to the functional group, and τ_2 the three more distant sites. All examples were run in CCl_4 on a Varian A-60 instrument employing a Me_4Si reference. [c] NE, neutralization equivalent.

and, after washing with dilute hydrochloric acid, tandem glc–mass spectroscopic analysis showed that all but approximately 10% of the chlorosilane had been reduced to the desired Me_3AdH. As is well known, ordinary chlorosilanes such as Me_3SiCl react almost instantaneously with nucleophiles such as water, ethereal $LiAlH_4$, etc.

To prepare a silylamine, Me_3AdCl was added to a hexane solution of the lithium salt of diethylamine prepared from the reaction of *n*-butyllithium in hexane with diethylamine. After 24 hr at room temperature the reaction was shown to be complete by glc assay. The silylamine reaction product was then extracted into dilute hydrochloric acid. The aminosilane was then recovered in 51% yield by adding excess NaOH and reextracting with fresh pentane. The survival of an Si–N bond under homogeneous aqueous acidic conditions such as the above is believed to be completely without precedent. Similar results were obtained with the analogous derivatives of various other amines including *n*-butylamine, *tert*-butylamine, and diethylamine.

Less dramatic, perhaps, but in a similar vein is the stability of the alkanolamine derivatives which can also be recovered unscathed from solution in aqueous hydrochloric acid. Thus, Me_3AdCl (2.8 g, 0.010 mol) was added to a solution of $LiOCH_2CH_2NMe_2$, prepared by the addition of $HOCH_2CH_2NMe_2$ (2.7 g, 0.03 mol) to 19 ml of 1.6 *M* *n*-BuLi in hexane (0.030 mol). Refluxing for 9 hr gave approximately 95% consumption of the starting Me_3AdCl (as evidenced by periodic glc assay). The resulting product mixture was extracted into 200 ml of 1% hydrochloric acid. Addition of LiOH regenerated the free base, $Me_3AdOCH_2CH_2NMe_2$, which was identified by glc and mass spectroscopy. The hydrolytic resistance of this type of aminoalkoxysilane is truly remarkable as indicated by the fact that it has undergone essentially no change after 3 months in 10% HCl at room temperature.

Both the aminoalkoxy and the amino derivatives such as $Me_3AdOCH_2CH_2NMe_2$ and Me_3AdNEt_2 can be readily converted to stable quaternary ammonium halides which, like the analogous hydrochloride salts, are very resistant to hydrolysis.[4] The salt containing the $Si-N^+R_3$ moiety is particularly interesting since thermolysis can yield either the halo or dialkylamino species depending on whether the halide ion displaces the nitrogen from the silicon or the carbon substituent; thermolysis on the heated probe of a mass spectrometer afforded the characteristic fragmentation for Me_3AdNEt_2 and methyl iodide, but no evidence for the formation of Me_3AdI and Et_2MeN.

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(4) $Me_3SiN^+ Me_3I^-$ was previously prepared [E. A. V. Ebsworth and H. J. Emeleus, *J. Chem. Soc.*, 2150 (1958)] but was presumably very susceptible to hydrolysis.

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The Mechanism of Interconversion of (*Z*)- and (*E*)-Ketimines

Sir:

Although there have been several investigations of the rate of interconversion of (*Z*)- and (*E*)-*N*-arylimines by the dynamic nmr method[1] (coalescence temperatures in the range 50–150°), the few reports on *N*-alkylimines indicate that interconversion is slow on the nmr time scale up to 180°.[2,3] We now report measurement of the interconversion rates of a series of *N*-alkylketimines at 180–200° by dynamic nmr spectroscopy (Table I). The stereochemistry of imines **1**, **2**, and **3** was assigned from the signal positions, the magnitude

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(1) For recent reviews see (a) J. M. Lehn, *Fortschr. Chem. Forsch.*, **15**, 311 (1970); (b) I. O. Sutherland, *Annu. Rep. Nucl. Magn. Resonance Spectrosc.*, **4**, 71 (1971); (c) C. G. McCarty in "The Chemistry of the Carbon–Nitrogen Double Bond," S. Patai, Ed., Interscience, London, 1969, p 363.

(2) D. Wurmb-Gerlich, F. Vögtle, A. Mannschreck, and H. A. Staab, *Justus Liebigs Ann. Chem.*, **708**, 36 (1967).

(3) N. P. Marullo and E. H. Wagener, *Tetrahedron Lett.*, 2555 (1969).