Table I. Spectral Data for Monofunctional Tetrasilaadamantanes, Me_3AdX

Compd	Mass spectrometry fragmentation[a] P	P − CH_3	P − X	Other	Nmr[b] τ_1	τ_2	Other	Ir, cm^{-1} (functional group)	Miscellaneous
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 ($SiOH$)	3685 (O–H)	Mp 135°
$Me_3AdOCH_2CH_2NMe_2$	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_2CH_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.

(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:

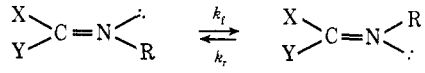
Although there have been several investigations of the rate of interconversion of (*Z*)- and (*E*)-*N*-arylimines by the dynamic nmr method[1] (coalescence temperatures in the range 50–150°), the few reports on *N*-alkylimines indicate that interconversion is slow on the nmr time scale up to 180°.[2,3] 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

(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).

Table I. Spectral Data (60 MHz) and Free Energy of Activation($\Delta G^{\pm}$) Determined at the Coalescence Temperature (T_c) for the Interconversion of (Z)- and (E)-Ketimines in Diphenyl Solution



Z E

Compd	X	Y	R	Obsd signals	$\Delta\nu$,[a] Hz at 60 MHz	T_c, °C	k_f,[b] sec^{-1}	k_r,[b] sec^{-1}	$\Delta G_f^{\pm}$, kcal mol^{-1}	$\Delta G_r^{\pm}$, kcal mol^{-1}
1	Me	1-Naphthyl	Me	CMe	17.4	200[c]	3.1	7.6	27.1	26.2
2	Me	1-Naphthyl	*i*-Pr	CMe_2	11.0	182	13	36	24.7	23.8
3	Et	Ph	CH_2Ph	CH_2Ph	12.6	199	22	14	25.2	25.6
4	Et	Et	CH_2Ph	Me	13.8	186	20	20	24.5	24.5
5	Ph	4-Nitrophenyl	Me	Me	6.8	191	9.2	4.7	25.5	26.1
6	Ph	4-Nitrophenyl	*t*-Bu	Me	4.9	89	8.2	3.7	19.8	20.4

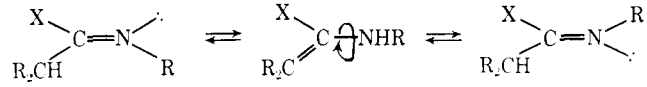
[a] Signal separation extrapolated to T_c and optimized to afford the best fit between calculated and observed spectra. [b] Site-exchange rates were determined directly from the spectra using a multisite computer program (INMR); in several cases *vicinal* or homoallylic coupling was present and was treated as producing additional sites of the appropriate relative intensity; see W. B. Jennings, *Chem. Commun.*, 867 (1971). [c] Maximum temperaturs attainable.

of the coupling constants [^4J(HCNCH)],[4] and by infrared spectroscopy (for **5** and **6**).[5]

The mechanism of interconversion of imine diastereomers is currently the subject of considerable debate, and has been considered[1] in terms of either a planar inversion mechanism or a rotation mechanism, with the latter probably involving a dipolar transition state.[6] Evidence obtained from studies of substituent effects (steric and electronic) suggests that *N*-arylimines interconvert by inversion[2,7] though the results have been considered to be inconclusive in view of the dependence of these effects on the conformation of the *N*-aryl moiety.[1a] In any case these results cannot readily be extrapolated to *N*-alkylimines in view of the known ability of an *N*-aryl group to facilitate nitrogen inversion in related pyramidal compounds.[1a,b] The $\Delta G^{\pm}$ values for imines **1**–**5** are remarkably insensitive to the nature of the carbon substituents, thus indicating that they interconvert by a mechanism close to pure nitrogen inversion as the energy of the dipolar (or diradical) transition state for rotation around the C=N bond would be considerably lowered by *C*-aryl substituents. The low barrier in **6** (relative to **5**) is probably a consequence of unfavorable nonbonded interactions in the ground state; steric acceleration of nitrogen inversion in pyramidal molecules is well established.[1a,b] Indeed, the difference in the $\Delta G^{\pm}$ values between compounds **5** and **6** is similar to the reported[8] lowering of the inversion barriers in diphenyloxaziridines by 6.4 kcal mol^{-1} when an *N*-methyl group is replaced by *N*-*tert*-butyl, thus providing further evidence that *N*-alkylketimines interconvert by inversion.

In addition to the two intramolecular mechanisms previously proposed, we suggest that a third mechanism should be considered where the imine contains a *C*-alkyl substituent with at least one α-hydrogen atom; (*Z*)- and (*E*)-imines of this type could interconvert by

Scheme I



tautomerization to the enamine (Scheme I).[9] The imines **3** and **4** which possess *C*-ethyl groups have been examined by nmr for evidence of this mechanism. In diphenyl solution at 200°, where *Z*–*E* interconversion is fairly fast on the nmr time scale, the CCH_2 protons were observed as a quartet (^3J(HCCH) ≈ 7.5 Hz). Tautomerization is therefore slow on the nmr time scale since fast proton exchange would lead to an observed loss of *vicinal* coupling. However, on heating a sample of **4** in 1,2,4-trichlorobenzene, the two ethyl groups coalesced at 140° to a single A_2M_3 system indicating that *Z*–*E* isomerization had become fast; on raising the temperature to 200° the CH_2 and CH_3 signals broadened again and collapsed to broad singlets consistent with rapid imine–enamine tautomerization.

A more definitive example where the tautomerism is more rapid than nitrogen inversion is provided by imines **1** and **2** which are available, by crystallization, in pure *Z* isomeric form (by a second-order diastereomeric transformation[10]). When the nmr spectrum was examined immediately after dissolution in deuteriomethanol at ambient temperature, the signals showed[11] that isomerization was proceeding with concomitant deuteration of the *C*-methyl group. This clearly demonstrates the dominance of the imine–enamine mechanism for *Z*–*E* interconversion (Scheme I) in this solvent. It is therefore clear that this isomerization mechanism should always be considered when dealing with compounds containing an HCC=N moiety.

(4) H. A. Staab, F. Vögtle, and A. Mannschreck, *Tetrahedron Lett.*, 697 (1965); D. A. Nelson and R. L. Atkins, *ibid.*, 5197 (1967); K. Tori, M. Ohtsuru, and T. Kubota, *Bull. Chem. Soc. Jap.*, **39**, 1089 (1966).

(5) D. Y. Curtin and J. W. Hausser, *J. Amer. Chem. Soc.*, **83**, 3474 (1961).

(6) Mechanisms intermediate between pure inversion and rotation are of course possible; see ref 1.

(7) D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Amer. Chem. Soc.*, **88**, 2775 (1966); A. Rieker and H. Kessler, *Tetrahedron*, **23**, 3723 (1967); G. Wettermark, *Ark. Kemi*, **27**, 159 (1967).

(8) F. Montanari, I. Moretti, and G. Torre, *Chem. Commun.*, 1086 (1969).

(9) Several examples of imine–enamine tautomerism have been reported; see M. Pfau and C. Ribière, *ibid.*, 66 (1970); R. A. Clark and D. C. Parker, *J. Amer. Chem. Soc.*, **93**, 7257 (1971).

(10) E. Carlson, F. B. Jones, Jr., and M. Raban, *Chem. Commun.*, 1235 (1969).

(11) Isomerization was followed by observing the appearance of the *N*-alkyl signals of the *E* isomer.

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