

(*m/e*) EI M<sup>+</sup> = 144, CI M + H = 145.

**Preparative Static Photolyses of 4-MDHN at 300 nm.** Static photolyses were performed on 4-MDHN with the following modifications. A 2-L Kimax round-bottom flask was attached to the static gas-phase apparatus (isolated from the main vacuum line via a vacuum valve), placed inside the gas-phase reactor, and filled with 300 mTorr of 4-MDHN. The gas was photolyzed at 300 nm for 2 h, and the products were then pumped into a trap cooled to -196 °C. Analysis by GLC on column D at 100–150 °C, using octadecane as an internal standard, indicated a total conversion of 4-MDHN of 12%. A total of 48 such photolyses (2–5 h each) were performed, the products were combined, and MVBCB was isolated by preparative GLC on column E at 140 °C

ramped to 180 °C. Analysis on column D at 100 °C showed 33.3% MVBCB and 65.9% T13B: <sup>1</sup>H NMR (ignoring the resonances of T13B) (CDCl<sub>3</sub>, 300 and 600 MHz) δ 7.06–7.25 (m, aromatic, 4 H), 6.17 (dd, *J*<sub>cis</sub> = 10.5 Hz, *J*<sub>trans</sub> = 17.2 Hz, vinyl CH, 1 H), 5.09 (dd, *J*<sub>gem</sub> = 1.7 Hz, *J*<sub>trans</sub> = 17.1 Hz, vinyl trans CH<sub>2</sub>, 1 H), 4.98 (dd, *J*<sub>gem</sub> = 1.6 Hz, *J*<sub>cis</sub> = 10.3 Hz, vinyl cis CH<sub>2</sub>, 1 H), 3.14 (d, *J* = 13.7 Hz, C2 CH<sub>2</sub> diastereomeric proton, 1 H), 3.03 (d, *J* = 13.7 Hz, C2 CH<sub>2</sub> diastereomeric proton, 1 H), 1.51 (s, CH<sub>3</sub>, 3 H); mass spectrum (capillary GLC/MS through column A) (*m/e*) EI M<sup>+</sup> = 144, CI M + H = 145.

**Acknowledgment.** We are grateful to the National Science Foundation (Grant CHE-8700333) for support of this research.

## Diadamantylsilylene and Its Stereochemistry of Addition

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**Abstract:** Lithium-induced dehalogenation assisted by ultrasonic irradiation of diadamantylidiodosilane in the presence of olefins and alkynes leads to high yields of 1,1-diadamantylsiliranes and 1,1-diadamantylsilirenes, respectively. The siliranes are precursors for the efficient thermal and photochemical generation of diadamantylsilylene (Ad<sub>2</sub>Si:). The addition of thermally generated Ad<sub>2</sub>Si: to *cis*- and *trans*-2-butene and -3-hexene is totally stereospecific, implying reaction from a singlet electronic state of the silylene. Photoisomerization of *cis*- and *trans*-1,1-diadamantylsiliranes complicates the study of the stereochemistry of addition of photogenic Ad<sub>2</sub>Si:, but again a high degree of stereospecificity is observed.

### Introduction

One of the original stimuli for the study of silylenes R<sub>2</sub>Si:, molecules containing divalent silicon atoms, the silicon analogues of carbenes, was the recognition that silylenes like carbenes should possess several low-lying excited states, each potentially displaying distinctive reactivity.<sup>1</sup> With no verified exceptions, silylenes, unlike carbenes, have singlet ground states. We suggested in 1984<sup>2</sup> that a fruitful approach to triplet ground-state silylenes might be the generation of silylenes with such bulky substituents that the bond angle would be greatly enlarged from the 92° found for :SiH<sub>2</sub>.<sup>3</sup> In the limit of linearity the nonbonding orbitals should be degenerate, and Hund's rule dictates a triplet ground state.

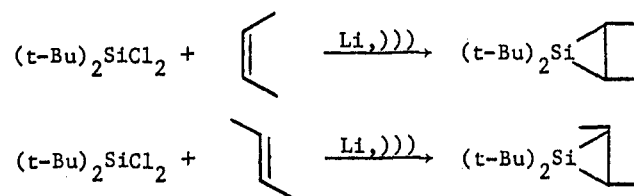
Ab initio calculations by Gordon predict that for unsubstituted SiH<sub>2</sub> the potential energy curves for the lowest singlet and triplet states cross at ca. 129°, with equilibrium bond angles of 93.38° for the singlet and 118.42° for the triplet.<sup>4</sup>

In the last few years, several sterically encumbered silylenes have been studied. Boudjouk and co-workers discovered the synthesis of siliranes via metal-promoted α-elimination of dihalosilanes.<sup>5</sup> Treatment of dichloro-di-*tert*-butylsilane in the presence of *cis*- and *trans*-butene under ultrasonic irradiation led to the stereospecific formation of 1,1-di-*tert*-butyl-2,3-dimethylsiliranes (Scheme 1).

The expected product of insertion of (*t*-Bu)<sub>2</sub>Si: into the H–Si bond of triethylsilane was obtained upon lithium-promoted dehalogenation of all three dihalosilanes (*t*-Bu)<sub>2</sub>SiX<sub>2</sub> examined (X = Cl, Br, I).<sup>5</sup> Since dehalogenation in the absence of a silylene trapping agent did not give the same products from the three dihalosilanes, Boudjouk concluded that a "silylenoid" was the reactive intermediate in at least one of the three cases.<sup>5</sup>

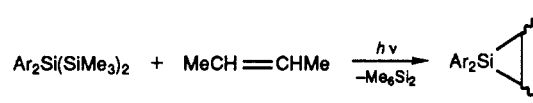
Boudjouk and co-workers made the important discovery that both photolysis and pyrolysis of *cis*- and *trans*-1,1-di-*tert*-butyl-2,3-dimethylsilirane lead to the extrusion of di-*tert*-butylsilylene ((*t*-Bu)<sub>2</sub>Si:).<sup>5</sup> The free silylene from silirane dissociation was trapped by insertion into H–Si, H–O, and addition to C≡C bonds. Boudjouk attributed these reactions to a singlet ground-state

### Scheme 1



silylene, although it is not clear that a triplet silylene would give different products from these reactions.

Ando and co-workers have studied the addition of bis(2,4,6-trialkylphenyl)silylenes to *cis*- and *trans*-2-butene.<sup>6</sup>



Ar = mesityl, 2, 4, 6-triisopropylphenyl

While addition of both di(mesityl)- and bis(2,4,6-triisopropylphenyl)silylene to *cis*-butene was nearly stereospecific, addition of both silylenes to *trans*-butene gave mixtures of *cis*- and *trans*-siliranes containing from 23 to 84% of the *cis* isomer. The largest yields of *cis* product were found in experiments in which the silylene was generated in a frozen matrix doped with *trans*-butene, and silylene addition was presumed to occur upon

(1) Gaspar, P. P. *Reactive Intermediates* (Wiley) 1978, 1, 229; 1981, 2, 335; 1985, 3, 333.

(2) Workshop on Organosilicon Reactive Intermediates, Sendai, Japan, Sept 16–18, 1984, discussion following presentation by P. Boudjouk, *Ultrasonic Waves and Reactive Organosilanes*.

(3) Dubois, I.; Herzberg, G.; Varma, R. D. *J. Chem. Phys.* 1967, 47, 4262.

(4) Gordon, M. S. *Chem. Phys. Lett.* 1985, 114, 348.

(5) Boudjouk, U.; Samaraweera, R.; Sooriyakumaran, J.; Chrusciel, Anderson, K. R. *Angew. Chem., Int. Ed. Engl.* 1988, 28, 1355.

(6) Ando, W.; Fujita, M.; Yoshida, H.; Sekiguchi, A. *J. Am. Chem. Soc.* 1988, 110, 3310.

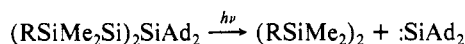
\* To whom correspondence should be addressed.

thawing of the matrix. This indicated that it was the ground state of the silylene that was undergoing addition. No triplet ESR signal was detected from the matrix-isolated silylenes at 77 K, and perhaps for this reason Ando did not make any mechanistic proposal to explain the observed nonstereospecificity of addition.

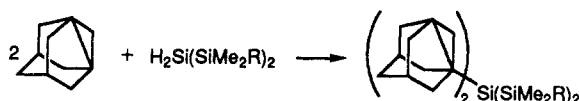
We thought that it would be of interest to study the reactions of diadamantylsilylene ( $\text{Ad}_2\text{Si}:$ ), hoping that its substituents would lend steric congestion sufficient to open up the bond angle at the divalent silicon to the point where the ground state would be a triplet.<sup>7</sup>

### Results and Discussion

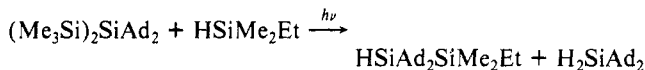
Our first attempts to generate diadamantylsilylene employed trisilane precursors whose photolysis was expected to extrude the desired  $\text{Ad}_2\text{Si}:$ .



Both these trisilanes were synthesized by a little-known novel "adamantylation" reaction, the hydrosilylation of 1,3-dehydroadamantane:<sup>8</sup>

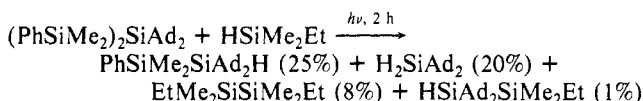


Irradiation of  $(\text{Me}_3\text{Si})_2\text{SiAd}_2$  with a medium-pressure mercury lamp in the presence of ethyldimethylsilane ( $\text{EtMe}_2\text{SiH}$ ) led to the formation of the product expected from  $\text{Ad}_2\text{Si}:$  Si-H insertion, plus a possible product of hydrogen abstraction, diadamantylsilane ( $\text{H}_2\text{SiAd}_2$ ):



While  $\text{H}_2\text{SiAd}_2$  could arise from hydrogen atom abstraction by triplet  $\text{Ad}_2\text{Si}:$ , the precursor absorbs weakly in the ultraviolet and requires long irradiation times. Hence, the possibility of radical processes had to be kept in mind.

The presence of phenyl chromophores led to the rapid photolysis of  $(\text{PhSiMe}_2)_2\text{SiAd}_2$  by use of the 254-nm radiation of a low-pressure mercury lamp. When this molecule was irradiated in the presence of  $\text{EtMe}_2\text{SiH}$ ,  $\text{H}_2\text{SiAd}_2$  was again formed as a major product and only a 1% yield of the  $\text{Ad}_2\text{Si}:$  H-Si insertion product was found:



The formation of  $(\text{EtMe}_2\text{Si})_2$  can be attributed to the dimerization of  $\text{EtMe}_2\text{Si}^{\cdot}$  radicals, and the product formed in highest yield,  $\text{PhSiMe}_2\text{SiAd}_2\text{H}$ , points to silicon-silicon bond homolysis or molecular elimination<sup>9</sup> as important primary steps in the photoreaction. The fragmentation of  $\text{PhSiMe}_2\text{SiAd}_2$  to  $\text{Ad}_2\text{Si}:$  must be regarded as unlikely on the basis of evidence presented against the fragmentation of a less crowded disilanyl radical.<sup>10</sup> Therefore, the formation of  $\text{H}_2\text{SiAd}_2$  in this reaction is likely to

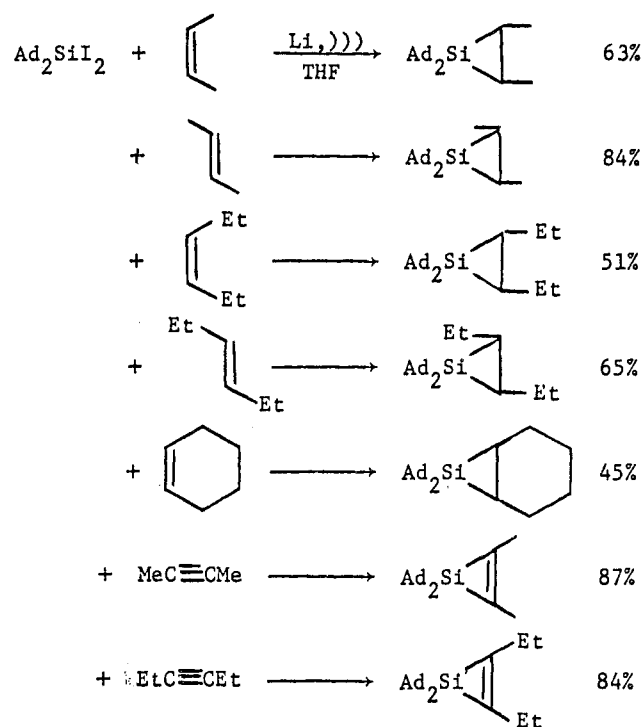
(7) A partially optimized MINDO/3 AMPAC calculation predicted a 124° bond angle.

(8) No, B. I.; Son, V. V.; Belyakova, T. V.; Ushchenko, V. P.; Kulikova, N. I. *Zh. Obshch. Khim.* **1982**, 52, 2138. Sasaki, T.; Shimizu, K.; Ohno, M. *Synth. Commun.* **1984**, 14, 853.

(9) Wilking, J. B.; Gaspar, P. P. *Photochemistry of 1,2-Dimesityltetramethyldisilane and 1,3-Dimesitylhexamethyltrisilane*, in preparation. Molecular elimination 27 ( $\pm 2$ )% and Si-Si bond homolysis 71 ( $\pm 7$ )% were the major primary photoprocesses in the 206-nm photolysis of hexamethyldisilane: Brix, Th.; Bastian, E.; Potzinger, P. *J. Photochem. Photobiol.* **1989**, 49, 287.

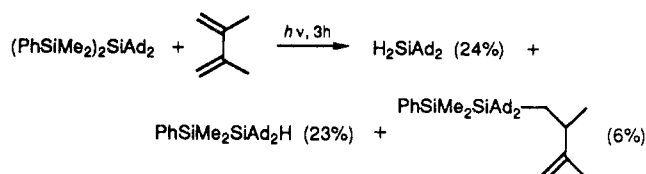
(10) Hawari, J. A.; Griller, D.; Weber, W. P.; Gaspar, P. P. *J. Organomet. Chem.* **1987**, 336, 335.

### Scheme II



be due to secondary photolysis processes rather than consecutive hydrogen abstraction by triplet  $\text{Ad}_2\text{Si}:$ . Attempts to detect a triplet ESR signal from photolysis of frozen glasses containing  $(\text{PhSiMe}_2)_2\text{SiAd}_2$  in the microwave cavity of an ESR spectrometer were unsuccessful.

Irradiation of  $(\text{PhSiMe}_2)_2\text{SiAd}_2$  in the presence of 2,3-dimethylbutadiene gave no 1-silacyclopent-3-ene, the product expected from addition of a singlet silylene, but again led to products ascribable to radical reactions:



While it can be argued that the formation of  $\text{H}_2\text{SiAd}_2$  and  $\text{PhSiMe}_2\text{SiAd}_2\text{H}$  in the presence of 2,3-dimethylbutadiene, an excellent radical scavenger, speaks for molecular elimination rather than free-radical pathways, the origin of  $\text{PhSiMe}_2\text{SiAd}_2\text{CH}_2\text{CHMeC}(\text{Me})=\text{CH}_2$  is surely addition of  $\text{PhSiMe}_2\text{SiAd}_2$  radicals.

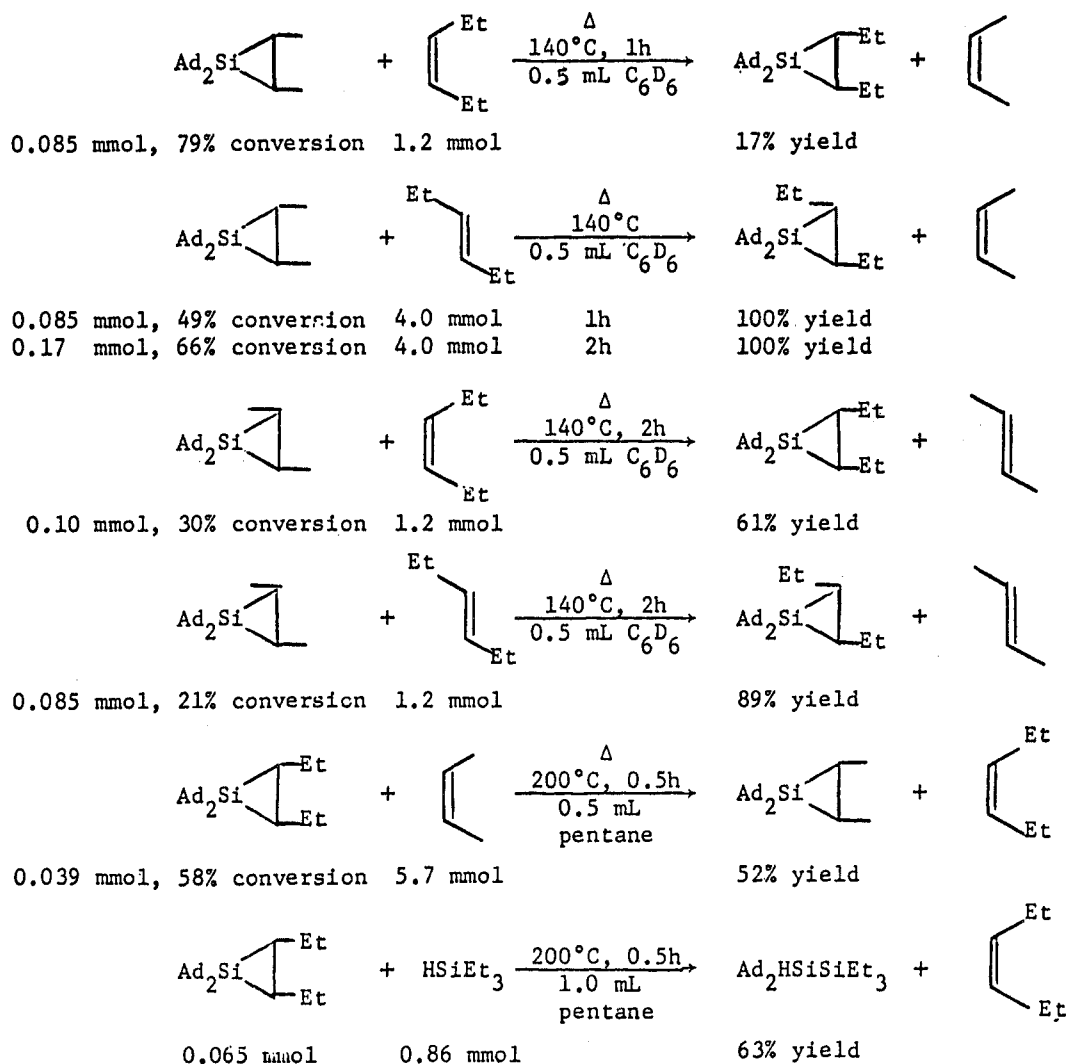
It was therefore decided to synthesize 1,1-diadamantylsiliranes as alternative silylene precursors, ample precedent being given by the pioneering work of Seyferth and co-workers on the thermalolysis of hexamethylsilirane<sup>11</sup> and in the thermal and photochemical decomposition of 1,1-di-*tert*-butylsiliranes by Boudjouk and co-workers.<sup>5</sup>

Diadamantylidiodosilane was synthesized by the uncatalyzed reaction of diiodosilane with 2 equiv of dehydroadamantane. Treatment of  $\text{Ad}_2\text{SiI}_2$  with lithium in the presence of olefins and alkynes under ultrasonic irradiation yielded the expected diadamantylsiliranes and -silirenes shown in Scheme II.

The 1,1-diadamantylsiliranes and -silirenes are rather stable. *cis*-1,1-Diadmantyl-2,3-dimethylsilirane can be heated for several hours at 80 °C without decomposition, which begins above 110 °C. Bubbling air through an NMR sample for 2 min did not alter the <sup>29</sup>Si NMR spectrum. Figure 1 is an ORTEP drawing of the

(11) Seyferth, D.; Annarelli, D. C. *J. Am. Chem. Soc.* **1975**, 97, 7162; *J. Organomet. Chem.* **1976**, 117, C51.

Scheme III. Thermolysis of 1,1-Diadamantylsiliranes in the Presence of Various Substrates



X-ray crystal structure of *trans*-1,1-diadamantyl-2,3-dimethylsilirane. The exocyclic C-Si-C bond angle is  $116.8^\circ$ , and the endocyclic angle is  $49.5^\circ$ .

Diadamantylsilylene ( $\text{Ad}_2\text{Si}$ ) is formed by extrusion from 1,1-diadamantyl-2,3-dialkylsiliranes upon pyrolysis or photolysis. Results are given in Schemes III-V.

The results given in Scheme III indicate that transfer of diadamantylsilylene from both *cis*- and *trans*-1,1-diadamantyl-2,3-dimethylsilirane to *cis*- and *trans*-3-hexene is, within experimental error (ca. 2%), completely stereospecific. Gas chromatographic and  $^1\text{H}$  NMR analysis of the reaction mixtures indicated that the 2-butene coproducts of silylene extrusion were also formed stereospecifically.

The more stable *cis*-1,1-diadamantyl-2,3-diethylsilirane undergoes an analogous reaction in which diadamantylsilylene is extruded stereospecifically and undergoes stereospecific addition to *cis*-2-butene. It should be noted that the yield is similar when the reaction substrate is triethylsilane, leading to the expected product of insertion of  $\text{Ad}_2\text{Si}$  into the H-Si bond of  $\text{HSiEt}_3$ . This latter reaction is unlikely to be a concerted *transfer* of the silylene group and can be assumed to occur via silylene extrusion, as was found by Seyferth in a series of careful experiments on hexamethylsilirane.<sup>12</sup>

Here, there are stereochemical labels suggesting that both the extrusion of diadamantylsilylene from the 1,1-diadamantylsiliranes whose thermolysis was examined and the addition to olefins forming diadamantylsiliranes are concerted. That in turn suggests,

according to the empirical generalization known as the Skell rule,<sup>13</sup> that in these silirane thermolyses  $\text{Ad}_2\text{Si}$  is formed and reacts in a singlet electronic state.

At a temperature of  $140^\circ\text{C}$ , some  $60^\circ\text{C}$  lower than that required for silylene extrusion from *cis*- and *trans*-1,1-diadamantyl-2,3-diethylsilirane, ca. 50% decomposition occurs in 1 h with or without the presence of reaction substrates, but complicated mixtures are formed, and no products could be identified.

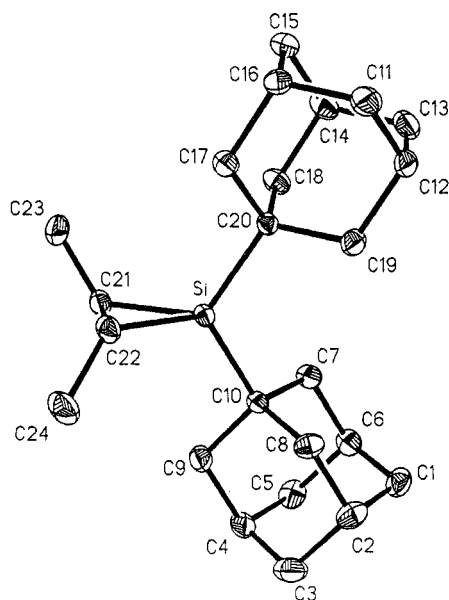
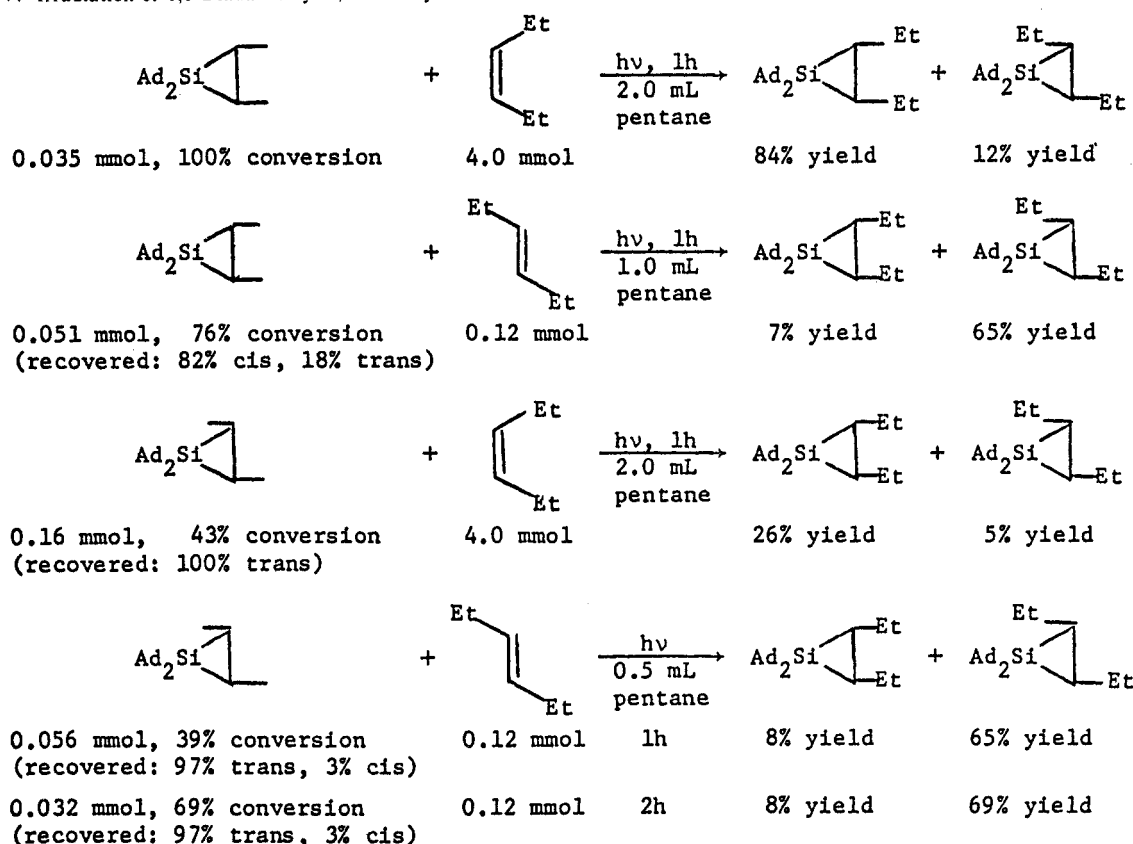
The photolysis of 1,1-diadamantylsiliranes presents a more complicated picture. Scheme IV reveals that photodissociation of *cis*- and *trans*-1,1-diadamantyl-2,3-dimethylsilirane in the presence of *cis*- and *trans*-3-hexene gives mixtures of the *cis*- and *trans*-stereoisomers of the  $\text{Ad}_2\text{Si}$  adduct. In all four cases, the predominant product stereoisomer retained the stereochemistry of the 3-hexene substrate, the retention varying from 84 to 90%. These results differ from those found by Ando for photochemically generated dimesityl- and bis(2,4,6-triisopropylphenyl)silylene, both of these diarylsilylenes seeming to show a high preference for the formation of the *cis* isomer of the 2-butene adduct.<sup>6</sup>

Scheme V shows similar results from the photolysis of *cis*- and *trans*-1,1-diadamantyl-2,3-diethylsilirane in the presence of *cis*- and *trans*-2-butene. Five of the six experiments with added olefin substrates gave mixtures in which the adduct stereoisomer with retained stereochemistry predominated to greater than 90%, with

(12) Seyferth, D.; Annarelli, D. C.; Duncan, D. P. *Organometallics* **1982**, *1*, 1288.

(13) Skell, P. S.; Woodworth, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 4496. For an examination of the assumptions underlying the Skell rule, see: Gaspar, P. P.; Hammond, G. S. In *Carbene Chemistry*, 1st ed.; Kirmse, W., Ed.; Academic Press: New York, 1964; p 235.

Scheme IV. Irradiation of 1,1-Diadamantyl-2,3-dimethylsiliranes in the Presence of Olefins



**Figure 1.** ORTEP drawing of the X-ray crystal structure of *trans*-1,1-diadamantyl-2,3-dimethylsilirane. Selected bond distances and angles: Si-C(21), 1.866 (4); Si-C(22), 1.867 (4); C(21)-C(22), 1.562 (6); Si-C(20), 1.911 (3); Si-C(10), 1.906 (4); C(10)-Si-C(20), 116.8 (1); C(21)-Si-C(22), 49.5 (2); Si-C(21)-C(22), 65.3 (2); Si-C(22)-C(21), 65.2 (2).

the remaining example giving only 75% retention. Recovered 1,1-diadamantyl-2,3-diethylsilirane has undergone significant *cis*-*trans* isomerization, from 17 to 42%. With no olefin substrate present, only 13% photoisomerization occurred during 1 h of irradiation and a considerable reduction in the conversion of the initial silirane was observed.

The results in Scheme V show that irradiation of the 1,1-diadamantyl-2,3-diethylsiliranes leads to a larger degree of *cis*-*trans* isomerization in the recovered starting material than the fraction

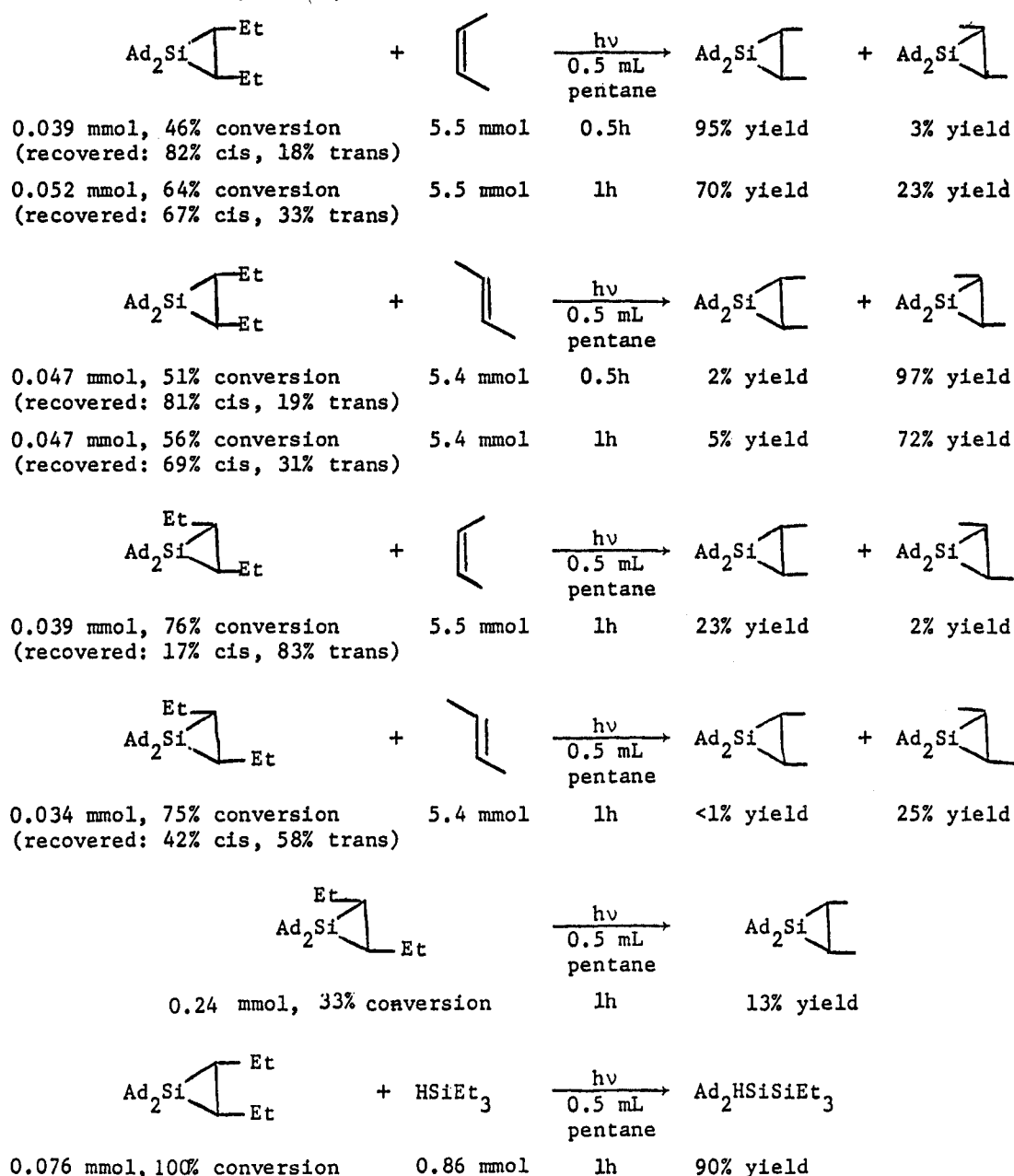
of the opposite stereoisomer found among the products from addition of photogenerated  $\text{Ad}_2\text{Si}\cdot$  to the 3-hexenes. This and the decreased conversion and photoisomerization in the absence of substrate are consistent with stereospecific  $\text{Ad}_2\text{Si}\cdot$  extrusion and addition, with photoisomerization being a separate process.

Comparison of Schemes IV and V indicates that the 1,1-diadamantyl-2,3-dimethylsiliranes are less prone to photoisomerization than the diethylsiliranes. Recovered dimethylsilirane that was initially *cis* contained 18% *trans* isomer after 76% photodissociation, and recovered dimethylsilirane that was initially *trans* contained only 3% *cis* isomer after 69% photodissociation. Thus, the degree of *cis*-*trans* isomerization in dimethylsiliranes recovered after irradiation is less than that for the diethylsiliranes. When dimethylsiliranes are the precursors for the photogeneration of  $\text{Ad}_2\text{Si}\cdot$  and diethylsiliranes are the products of  $\text{Ad}_2\text{Si}\cdot$  addition, the products are more susceptible to *cis*-*trans* photoisomerization than the starting materials. Therefore, the degree of nonstereospecificity observed for the addition of  $\text{Ad}_2\text{Si}\cdot$  photogenerated by extrusion from 1,1-diadamantyl-2,3-dimethylsiliranes is slightly higher than that observed for the diethylsiliranes as  $\text{Ad}_2\text{Si}\cdot$  precursors.

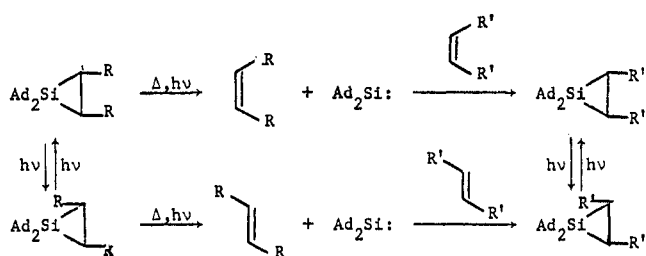
Under this interpretation, the photochemical as well as the thermal experiments support a mechanism shown in Scheme VI in which diadamantylsilylene is extruded stereospecifically from 1,1-diadamantylsiliranes and undergoes concerted addition to olefins, forming new 1,1-diadamantylsiliranes. That the thermal and photochemical decomposition of the 1,1-diadamantylsiliranes leads to free diadamantylsilylene is indicated by the high yields of H-Si insertion product obtained when triethylsilane is the reaction substrate. The stereospecific formation of and addition by  $\text{Ad}_2\text{Si}\cdot$  speak for a singlet electronic state. Photochemical *cis*-*trans* isomerization of 1,1-diadamantyl-2,3-dialkylsiliranes seems to be an independent process, possibly mediated by a diradical intermediate.

1,1-Diadamantylsiliranes arise from the addition of thermally generated  $\text{Ad}_2\text{Si}\cdot$  to acetylenes. Competition between an alkyne and a silane allowed a comparison of the selectivity of the reactive intermediates formed from photolysis and pyrolysis of 1,1-di-

Scheme V. Irradiation of 1,1-Diadamantyl-2,3-diethylsiliranes



Scheme VI



adamantylsilyliranes with those formed upon lithium-induced deiodination of  $\text{Ad}_2\text{SiI}_2$ . Results are given in Scheme VII.

The predominance of Si-H insertion, accompanied by some reduction, in the room-temperature metal-induced reaction contrasts with the preponderance of  $\pi$ -addition observed in the room-temperature photolysis and high-temperature pyrolysis. While  $\pi$ -addition is favored, there are differences between the selectivity observed in the photolysis and pyrolysis experiments, although both conditions are believed to produce free  $\text{Ad}_2\text{Si:}$ . These differences may be due to a temperature dependence of the

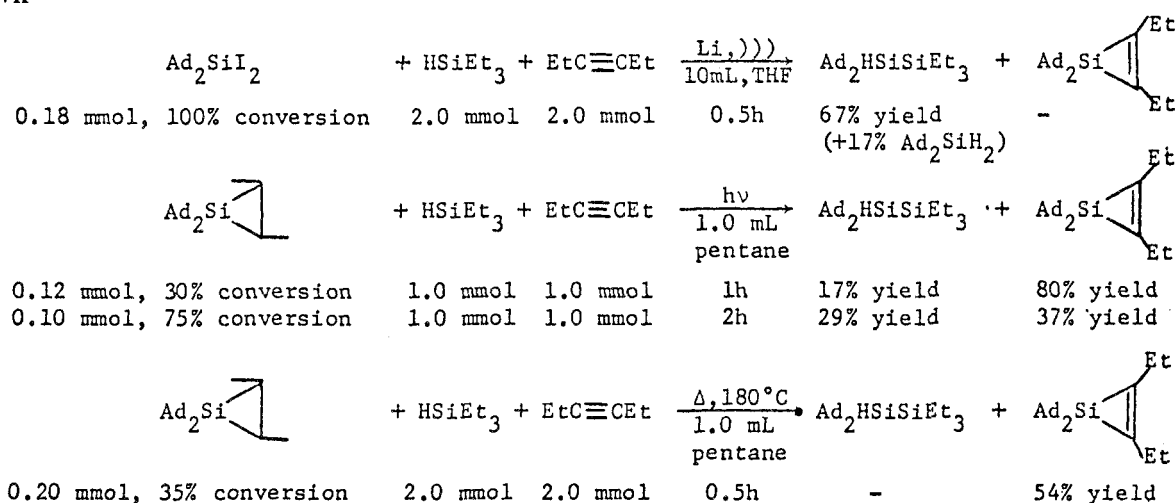
rate constants for  $\text{Ad}_2\text{Si:}$  insertion or addition reactions. Another explanation is required for the selectivity *inversion* relative to both photolysis and pyrolysis observed in the lithium-promoted dehalogenation. The selectivity inversion may be due to the involvement of different reactive intermediates: free  $\text{Ad}_2\text{Si:}$  in the silirane photolysis and pyrolysis and a silylenoid  $\text{Ad}_2\text{SiLi}$  or  $\text{Ad}_2\text{Si}(\text{THF})$  in the metal-induced reaction, as suggested by Boudjouk.<sup>5</sup>

If the reactive intermediate formed upon lithium-promoted deiodination of  $\text{Ad}_2\text{SiI}_2$  is a silylenoid, as suggested above, it nevertheless mimics silylenes closely, even inserting into an Si-H bond.

### Conclusion

Diadamantylsilyliranes have been synthesized by lithium-induced, ultrasound-promoted dehalogenation of diadamantylidiodosilane and have been shown to act as precursors for the efficient thermal and photochemical generation of diadamantylsilylene ( $\text{Ad}_2\text{Si:}$ ). The high degree of stereospecificity of the diadamantylsilylirane decomposition and diadamantylsilylene-olefin addition reactions speaks for the concerted formation and subsequent reactions of a singlet ground-state silylene.

## Scheme VII



The reactive intermediate formed upon treatment of  $\text{Ad}_2\text{I}_2$  with lithium undergoes stereospecific addition to olefins, insertion into the H-Si bond of  $\text{HSiEt}_3$ , and addition to alkynes yielding 1,1-diadamantylsilanes, as does free  $\text{Ad}_2\text{Si}$ : extruded from siliranes. That the reactive intermediate in the lithium reaction is not free  $\text{Ad}_2\text{Si}$ : is indicated by selectivity differences found in competition experiments.

This work, taken in connection with Boudjouk's success in generating di-*tert*-butylsilylene ( $(t\text{-Bu})_2\text{Si}$ ) from a corresponding silirane,<sup>5</sup> suggests that the thermolysis and photolysis of siliranes with bulky substituents at silicon are the most efficient and synthetically tractable general routes to a variety of silylenes. It is expected that this approach will succeed in attaining ground-state triplet silylenes very soon.

## Experimental Section

**General Data.** All preparative reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen or argon. Unless otherwise specified, photolyses were carried out in a Rayonet RS photochemical reactor equipped with low-pressure mercury lamps emitting 254-nm radiation. All solvents were dried by and distilled from, benzophenone sodium ketyl under a nitrogen atmosphere just prior to use.

$^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra were recorded on Varian XL-300 and Gemini-300 FT spectrometers. Combined gas chromatography-mass spectrometry was performed on a Finnigan 3200 mass spectrometer operating at an ionizing energy of 70 eV. High-resolution mass spectra were recorded on a VG-ZAB-SE double-focusing mass spectrometer. Mass spectra were calibrated against perfluoroalkane internal standards. Analytical gas chromatography was carried out on a Hewlett-Packard Model 5890 Series II instrument with a flame ionization detector employing a 15 ft  $\times$  1/8 in. (i.d.) stainless steel column with 3% OV-17 on Chromosorb W packing.

Reported yields are based on the unrecovered silylene or silylenoid precursor and were determined by integration of the  $^1\text{H}$  NMR spectrum with the use of dodecamethylcyclohexasilane as an internal standard. In each case, peaks with no interferences or overlaps were selected for yield measurements.

**Materials.** Adamantane (Aldrich, >99%), *cis*-2-butene (Matheson, >95%), *trans*-2-butene (Matheson, >95%), 2-butyne (Aldrich, 99%), chlorodimethylphenylsilane (Petrarch), cyclohexene (Aldrich, 99%), dichlorosilane (Petrarch, 98%), ethyldimethylchlorosilane (Petrarch), *trans*-3-hexene (Aldrich, >99%), 3-hexyne (Aldrich, 99%), and triethylsilane (Aldrich, 99%) were employed as received.

**1,3-Dehydroadamantane.** The compound was synthesized by the method of Pincock and co-workers.<sup>14</sup>

**2,2-Diphenyl-1,1,1,3,3,3-hexamethyltrisilane.** The compound was synthesized by the method of Jones and co-workers.<sup>15</sup>

**Diiodosilane.** The compound was synthesized by the method of Keinan and Perez.<sup>16</sup>

**Ethyldimethylsilane.** The compound was synthesized by reduction of  $\text{EtMe}_2\text{SiCl}$  with  $\text{LiAlH}_4$ .<sup>17</sup>

***cis*-3-Hexene.** The compound was synthesized by the method of Brown and Zweifel.<sup>18</sup>

**2,2-Dichloro-1,1,1,3,3,3-hexamethyltrisilane.** In a 500-mL three-necked, round-bottomed flask equipped with a magnetic stirring bar, a reflux condenser, and a gas-bubbling inlet tube were placed 42.5 g (0.13 mol) of 2,2-diphenyl-1,1,1,3,3,3-hexamethyltrisilane, 250 mL of benzene, and 2 g of  $\text{AlCl}_3$ . While the solution was stirred rapidly, dry gaseous  $\text{HCl}$  was bubbled through the solution until, after ca. 3 h, monitoring by gas chromatography indicated that chlorodephenylation was complete. Nitrogen was bubbled through the reaction mixture to remove dissolved  $\text{HCl}$ , and benzene was removed under reduced pressure. Fractional distillation at 10 Torr gave 24.5 g (78% yield) of 2,2-dichloro-1,1,1,3,3,3-hexamethyltrisilane: bp 75–77 °C (10 Torr) (lit.<sup>19</sup> bp 75–78 °C (10 Torr));  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.14.

**1,1,1,3,3,3-Hexamethyltrisilane.** The compound was synthesized by  $\text{LiAlH}_4$  reduction of 2,2-dichloro-1,1,1,3,3,3-hexamethyltrisilane by the method of Boo.<sup>20</sup>

**1,3-Diphenyl-1,1,3,3-tetramethyltrisilane.** Wurtz coupling of  $\text{PhSiMe}_2\text{Li}$  and  $\text{Cl}_2\text{SiH}_2$  was carried out. Fine-cut lithium metal (14 g, 2.0 mol) and 300 mL of THF were placed in a 1000-mL three-necked flask equipped with a mechanical stirrer, reflux condenser, and an additional funnel containing a mixture of 85 g (0.5 mol) of chlorodimethylphenylsilane and 100 mL of THF. While the mixture was stirred under nitrogen, 25 mL of the  $\text{PhSiMe}_2\text{Cl}$  solution was added to the reaction flask. After a few minutes, the reaction mixture became warm and a red color developed. The remainder of the  $\text{PhSiMe}_2\text{Cl}$  solution was added dropwise over 2 h, and a dark red solution was found after the reaction mixture was stirred overnight. This solution was transferred to a large addition funnel and added dropwise to a solution of dichlorosilane (25 g, 0.25 mol) in 150 mL of THF prepared by condensing the  $\text{Cl}_2\text{SiH}_2$  in a 1000-mL three-necked flask containing the THF and cooled with an acetone-dry ice bath. The reaction mixture was allowed to warm slowly to room temperature, and after overnight stirring the red color had changed to yellow. Solvent was removed under vacuum in a rotary evaporator, and the remaining material was mixed with 200 mL of pentane and filtered to remove lithium chloride. After evaporation of the pentane from the filtrate, fractional distillation gave 42.1 g (0.14 mol, 55% yield) of 1,3-diphenyl-1,1,3,3-tetramethyltrisilane: bp 139–142 °C (0.4 Torr);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.33 (s, 12 H, Me), 3.28 (s, 2 H,  $\text{SiH}_2$ ), 7.15–7.16 (m, 6 H, Ph), 7.41–7.42 (m, 4 H, Ph).

**2,2-Diadmantyl-1,1,1,3,3,3-hexamethyltrisilane.** A 50-mL three-necked flask equipped with a magnetic stirring bar, a glass stopper, and two rubber septa was loaded in a drybox with 1.0 g (80% purity, 6.0 mmol) of 1,3-dehydroadamantane and 10 mL of hexane under a nitrogen atmosphere. After the flask was brought out of the box, 0.5 g (2.8 mmol) of 1,1,1,3,3,3-hexamethyltrisilane and 10  $\mu\text{L}$  of 0.1 M  $\text{H}_2\text{PtCl}_6$  solution in *i*-PrOH were sequentially added via syringes through the septa. The septa were rapidly replaced by a reflux condenser and nitrogen inlet, and the reaction mixture was stirred and refluxed for 12 h. After the reaction mixture was allowed to cool, air was bubbled through it for 30 min,

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leading to a white precipitate of a peroxide formed from excess dehydroadamantane, removed by filtration. After evaporation of solvent from the filtrate, 1.1 g of white solid (89% crude yield) was obtained giving, after recrystallization from EtOH, 1.0 g (79% yield) of 2,2-diadamantyl-1,1,1,3,3,3-hexamethyltrisilane: mp 221–224 °C;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.37 (s, 18 H, SiMe<sub>3</sub>), 1.75 (s, 12 H Ad CH<sub>2</sub>), 1.85 (s, 6 H, Ad CH), 2.10 (s, 12 H, Ad CH<sub>2</sub>);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 75 MHz)  $\delta$  3.6, 29.0, 29.5, 37.9, 42.3; MS  $m/e$  (relative intensity) 445 ( $\text{M}^+$ , 1.7), 444 (1.0), 372 (11), 310 (1.2), 136 (100), 135 (97); exact mass determination for  $\text{C}_{26}\text{H}_{48}\text{Si}_3$  ( $\text{M}^+$ ), calcd 444.3064, found 444.3055.

**2,2-Diadamantyl-1,1,3,3-tetramethyl-1,3-diphenyltrisilane.** The compound was synthesized by the procedure described above for 2,2-diadamantyl-1,1,1,3,3,3-hexamethyltrisilane, employing 1.9 g (80% purity, 11.7 mmol) of 1,3-dehydroadamantane, 30 mL of hexane, 1.8 g (6.0 mmol) of 1,1,3,3-tetramethyl-1,3-diphenyltrisilane, and 10  $\mu\text{L}$  of 0.1 M  $\text{H}_2\text{PtCl}_6$  in *i*-PrOH. A 3.3-g (97% crude yield) of white solid was recrystallized from EtOH, giving 3.2 g (93% yield) of 2,2-diadamantyl-1,1,3,3-tetramethyl-1,3-diphenyltrisilane: mp 173–175 °C;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.67 (s, 12 H, SiMe<sub>3</sub>), 1.71 (s, 12 H, Ad CH<sub>2</sub>), 1.81 (s, 6 H, Ad CH), 2.06 (s, 12 H, Ad CH<sub>2</sub>), 7.20 (m, 6 H, Ph), 7.65 (d, 6 H, Ph);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 75 MHz)  $\delta$  2.6, 29.0, 30.2, 37.7, 41.8, 128 (m), 135.5; MS  $m/e$  (relative intensity) 569 ( $\text{M}^+$ , 1.0), 568 (1.1), 434 (35), 299 (33), 136 (100), 135 (98); exact mass determination for  $\text{C}_{36}\text{H}_{52}\text{Si}_3$  ( $\text{M}^+$ ), calcd 568.3376, found 568.3366.

**Diadamantyldiiodosilane (Ad<sub>2</sub>SiI<sub>2</sub>).** In a drybox, 5.0 g (80% purity, the remainder adamantane, 30 mmol) of 1,3-dehydroadamantane and 25 mL of pentane were loaded into a 50-mL round-bottom flask under a nitrogen atmosphere. The sleeve-stoppered flask was brought out from the drybox and cooled in an ice bath. With a syringe, 4.1 g (14.4 mmol) of diiodosilane ( $\text{H}_2\text{SiI}_2$ ) was added. The solution became warm, and a white precipitate formed immediately. With the rubber septum replaced by a reflux condenser equipped with an inlet tube for an argon atmosphere, the reaction mixture was refluxed for 2 h. The white solid product was isolated by filtration under a nitrogen atmosphere and was washed with pentane and dried under vacuum, giving 6.85 g (87% yield). The diadamantyldiiodosilane was kept in a cool, dry, dark place:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.46–1.58 (m, 12 H), 1.73 (s, 6 H), 2.02 (s, 12 H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 75.4 MHz)  $\delta$  28.3, 37.2, 38.7;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 59.6 MHz, INEPT)  $\delta$  35.3; exact mass determination for  $\text{C}_{20}\text{H}_{30}\text{I}_2\text{Si}_2$  ( $\text{M}^+$ ), calcd 552.0205, found 552.0206.

**Diadamantylsilane.** To a solution of 1.0 g (1.8 mmol) of  $\text{Ad}_2\text{SiI}_2$  and 25 mL of THF in a 50-mL three-necked flask fitted with a reflux condenser and nitrogen inlet and a magnetic stirring bar was added 0.4 g (10.5 mmol) of  $\text{LiAlH}_4$ , and the reaction mixture was stirred for 1 h. Excess  $\text{LiAlH}_4$  was destroyed with water, and the product was extracted with two 20-mL portions of hexane. After the solution was dried over  $\text{CaCl}_2$ , solvent was evaporated, giving 0.46 g (85% yield) of white solid  $\text{Ad}_2\text{SiH}_2$ , needlelike crystals after recrystallization from hexane: mp 112–115 °C;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.73 (s, 12 H, CH<sub>2</sub>), 1.81 (s, 6 H, CH), 1.89 (s, 12 H, CH<sub>2</sub>), 3.42 (s, 2 H, SiH<sub>2</sub>);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 75 MHz)  $\delta$  23.5, 28.2, 73.6, 40.3; MS  $m/e$  (relative intensity) 300 ( $\text{M}^+$ , 1.9), 165 (13), 135 (100); exact mass determination for  $\text{C}_{20}\text{H}_{32}\text{Si}$  ( $\text{M}^+$ ), calcd 300.2372, found 300.2273.

**1,1-Diadamantyl-2,2,2-triethyldisilane.** A mixture of 0.22 g (0.4 mmol) of diadamantyldiiodosilane, 0.7 g of finely cut lithium metal, and 0.46 g (0.4 mmol) of triethylsilane in 20 mL of THF was sonicated 1 h in an ultrasonic bath. The reaction mixture, originally a cloudy suspension, became clear, and a gray precipitate formed. The precipitate and unreacted lithium were removed by filtration, the filtrate was washed with water and diluted with pentane, and the organic phase was dried over sodium sulfate. After evaporation of solvent and unreacted triethylsilane, 150 mg (90% yield) of 1,1-diadamantyl-2,2,2-triethyldisilane was obtained as a white solid: mp 85–86 °C;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.88 (q, 6 H,  $J$  = 7.9 Hz, Et CH<sub>3</sub>), 1.11 (t, 9 H,  $J$  = 7.9 Hz, Et CH<sub>2</sub>), 1.78–2.02 (m, 30 H, Ad), 3.42 (s, 1 H, SiH);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 75.4 MHz)  $\delta$  5.6, 8.1, 26.2, 28.1, 37.3, 41.3;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 59.6 MHz, INEPT)  $\delta$  -11.2, -7.0. Anal. Calcd for  $\text{C}_{26}\text{H}_{46}\text{Si}_2$ : C, 75.28; H, 11.18. Found: C, 74.73; H, 11.18.

***cis*-1,1-Diadamantyl-2,3-dimethylsilirane.** A suspension of 0.62 g (1.1 mmol) of  $\text{Ad}_2\text{SiI}_2$  and 0.15 g of freshly cut Li in 30 mL of THF was degassed on a Schlenk line, and 3 mL of *cis*-2-butene was condensed into the reaction flask. After 30 min of sonication, the reaction mixture turned clear yellow, the reaction flask was moved into a drybox, and solvent was evaporated in vacuo. Pentane was added to dissolve the product, and the mixture was filtered through a small column packed with silica gel to remove LiI. Evaporation of solvent from the filtrate gave 0.25 g (63% yield) of *cis*-1,1-diadamantyl-2,3-dimethylsilirane as a white solid:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.07 (m, 2 H, silirane CH), 1.50 (m, 6 H, silirane Me), 1.73–2.16 (m, 30 H, Ad);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 75.4 MHz)  $\delta$  8.1, 10.1, 24.1, 28.1, 37.2, 37.3, 40.2, 41.7;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ,

59.6 MHz, INEPT)  $\delta$  -63.6; UV ( $\text{C}_6\text{H}_{12}$ ) no maximum >200 nm,  $\epsilon$  = 129 at 254 nm. Anal. Calcd for  $\text{C}_{24}\text{H}_{38}\text{Si}$ : C, 81.28; H, 10.80. Found: C, 80.89; H, 10.94.

***trans*-1,1-Diadamantyl-2,3-dimethylsilirane.** The procedure was the same as that for the *cis* isomer, employing 0.74 g (1.3 mmol) of  $\text{Ad}_2\text{SiI}_2$ , 0.15 g of Li, and 5 mL of *trans*-2-butene and yielding 0.40 g (84% yield) of product as a white solid:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.66 (m, 2 H, silirane CH), 1.56 (m, 6 H, silirane Me), 1.74–2.03 (m, 30 H, Ad);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 75.4 MHz) 15.5, 16.5, 25.6, 28.1, 37.3, 41.2;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 59.6 MHz, INEPT)  $\delta$  -53.8; UV ( $\text{C}_6\text{H}_{12}$ ) no maximum >200 nm,  $\epsilon$  = 323 at 254 nm.

**X-ray Analysis.** *trans*-1,1-Diadamantyl-2,3-dimethylsilirane was recrystallized from pentane at -40 °C, and the crystals were isolated as colorless plates,  $\text{C}_{24}\text{H}_{30}\text{Si}$  (FW = 354.65): monoclinic,  $P2_1/n$ ,  $a$  = 11.172 (6) Å,  $b$  = 16.7877 Å,  $c$  = 99.12 (4) Å,  $V$  = 2098 (2) Å<sup>3</sup>,  $Z$  = 4, Mo  $K\alpha$  radiation ( $\lambda$  = 0.71069 Å), 295 K, Siemens R3m/V diffractometer with graphite monochromator; 5223 reflections were collected ( $3.5 \leq 2\theta \leq 55.0$ ) by use of  $2\theta$  scans. Of these, 4805 reflections were unique ( $R_{\text{int}}$  = 0.85%) and 2372 were considered observed ( $F > 6.0\sigma(F)$ ). The structure was solved by Siemens SHELXTL PLUS and refined by full-matrix least-square to  $R$  = 0.0516 and  $R_w$  = 0.0515.

***cis*-1,1-Diadamantyl-2,3-diethylsilirane.** A mixture of 1.0 g (1.8 mmol) of  $\text{Ad}_2\text{SiI}_2$ , 0.1 g of Li, and 0.8 g (9.5 mmol) of *cis*-3-hexene in 20 mL of THF was sonicated for 45 min. After workup as described above, 0.35 g (51% yield) of product was obtained as a white solid:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.98 (m, 2 H, silirane CH), 1.19 (t, 6 H,  $J$  = 7.1 Hz, Et CH<sub>3</sub>), 1.73–2.12 (m, 34 H, Ad and Et CH<sub>2</sub>);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 75.4 MHz)  $\delta$  18.2, 19.4, 19.7, 24.3, 28.5, 28.6, 37.6, 37.7, 40.8, 41.9;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 59.6 MHz, INEPT)  $\delta$  -62.6.

***trans*-1,1-Diadamantyl-2,3-diethylsilirane.** A mixture of 0.5 g (0.9 mmol) of  $\text{Ad}_2\text{SiI}_2$ , 0.1 g of Li, and 0.8 g (9.5 mmol) of *trans*-3-hexene in 20 mL of THF was sonicated for 45 min and gave, after workup, 0.23 g (65% yield) of white solid product:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.67 (m, 2 H, silirane CH), 1.18 (t, 6 H,  $J$  = 7.3 Hz, Et CH<sub>3</sub>), 1.73–2.02 (m, 34 H, Ad and Et CH<sub>2</sub>);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 75.4 MHz)  $\delta$  17.1, 24.4, 25.5, 25.8, 28.1, 37.3, 41.3;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 59.6 MHz, INEPT)  $\delta$  -53.8.

**1,1-Diadamantyl-1-silanorcarane.** A mixture of 0.72 g (1.3 mmol) of  $\text{Ad}_2\text{SiI}_2$ , 0.1 g of Li, and 0.5 g (6 mmol) of freshly distilled cyclohexene in 20 mL of THF was sonicated for 30 min and gave, after workup, 0.22 g (45% yield) of white solid product:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.05 (m, 2 H), 1.73–1.90 (m, 32 H), 2.20 (s, 6 H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 75.4 MHz)  $\delta$  11.1, 19.6, 23.4, 24.6, 28.5, 28.5, 37.6, 37.7, 40.5, 42.0;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 59.6 MHz, INEPT)  $\delta$  -66.5.

**1,1-Diadamantyl-2,3-dimethylsilirene.** A mixture of 0.70 g (1.3 mmol) of  $\text{Ad}_2\text{SiI}_2$ , 0.05 g of Li, and 0.35 g (6.5 mmol) of 2-butyne in 20 mL of THF was sonicated for 30 min and gave, after workup, 0.40 g (87% yield) of white solid product:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.76 (m, 12 H), 1.84 (m, 6 H), 1.94 (m, 12 H), 2.22 (6, 6 H);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 75.4 MHz)  $\delta$  13.4, 27.1, 28.2, 41.0, 146.6;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 59.6 MHz, INEPT)  $\delta$  -73.1.

**1,1-Diadamantyl-2,3-diethylsilirene.** A mixture of 0.38 g (0.7 mmol) of  $\text{Ad}_2\text{SiI}_2$ , 0.1 g of Li, and 0.10 g (1.2 mmol) of 3-hexyne in 15 mL of THF was sonicated for 45 min and gave, after workup, 0.22 g (84% yield) of white solid product:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.19 (t, 6 H,  $J$  = 7.4 Hz, Et CH<sub>3</sub>), 1.76 (m, 12 H, Ad), 1.84 (m, 6 H, Ad), 1.93 (m, 12 H, Ad), 2.48 (q, 4 H,  $J$  = 7.4 Hz, Et CH<sub>2</sub>);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 75.4 MHz)  $\delta$  15.6, 22.7, 27.1, 28.7, 37.8, 41.6, 151.0;  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 59.6 MHz, INEPT)  $\delta$  -71.6.

**Photolysis of 2,2-Diadamantyl-1,1,1,3,3,3-hexamethyltrisilane in the Presence of Ethyldimethylsilane.** Into a quartz photolysis tube equipped with a Teflon stopcock was placed a mixture of 0.1 g of  $(\text{Me}_2\text{Si})_2\text{SiAd}_2$  and 1.0 g of  $\text{EtMe}_2\text{SiH}$  dissolved in 10 mL of pentane. After being degassed on a vacuum line to 0.02 Torr, the sample was irradiated for 24 h with a Hanovia 450-W medium-pressure mercury lamp. After irradiation, solvent and excess  $\text{EtMe}_2\text{SiH}$  were evaporated in vacuo, and the products were separated by thin-layer chromatography on silica gel with pentane as eluent. Diadamantylsilane and 1,1-diadamantyl-2-ethyl-2,2-dimethyldisilane were obtained in yields of ca. 10% and 20%, respectively.  $\text{HSiAd}_2\text{SiEtMe}_2$ :  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.37 (s, 6 H SiMe), 0.87 (m, 3 H, Et CH<sub>3</sub>), 1.24 (m, 6 H, Et CH<sub>2</sub>), 1.77 (m, 12 H, Ad), 1.85 (m, 6 H, Ad), 2.02 (m, 6 H, Ad), 2.10 (s, 6 H, Ad), 3.34 (d, 1 H, SiH); MS  $m/e$  (relative intensity) 386 ( $\text{M}^+$ , 10), 371 (2.3), 251 (94), 135 (100).

**Photolysis of 2,2-Diadamantyl-1,1,3,3-tetramethyl-1,3-diphenyltrisilane in the Presence of Ethyldimethylsilane or 2,3-Dimethylbutadiene.** Into a quartz photolysis tube equipped with a Teflon stopcock was placed a mixture of 0.1 g of  $(\text{PhSiMe}_2)_2\text{SiAd}_2$  and 1.0 g of  $\text{EtMe}_2\text{SiH}$  or of 2,3-dimethylbutadiene. After being degassed on a vacuum line to 0.02 Torr, the sample tube was irradiated in the Rayonet photochemical reactor with low-pressure mercury lamps for 2 h. After irradiation,

solvent and excess substrate were evaporated in vacuo, and the products were separated by thin-layer chromatography on silica gel with pentane eluent. The products obtained in the presence of  $\text{EtMe}_2\text{SiH}$  (93% conversion of starting material) were  $\text{Ad}_2\text{SiH}_2$  (22%),  $\text{PhSiMe}_2\text{SiAd}_2\text{H}$  (27%),  $(\text{EtMe}_2\text{Si})_2$  (9%), and  $\text{HSiAd}_2\text{SiEtMe}_2$  (1%). In the presence of 2,3-dimethylbutadiene, the products were  $\text{Ad}_2\text{SiH}_2$  (24%),  $\text{PhSiMe}_2\text{SiAd}_2\text{H}$  (23%), and  $\text{PhSiMe}_2\text{SiAd}_2\text{CH}_2\text{CHMeCMe}=\text{CH}_2$  (6%).

**PhSiMe<sub>2</sub>SiAd<sub>2</sub>H:**  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.57 (s, 6 H, SiMe), 1.71 (m, 12 H, Ad), 1.79 (m, 6 H, Ad), 1.96 (m, 12 H, Ad), 3.48 (s, 1 H, SiH), 7.22 (m, 3 H, Ph), 7.62 (m, 2 H, Ph).

**(EtSiMe<sub>2</sub>)<sub>2</sub>:**  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.01 (s, 12 H, SiMe), 0.58 (q, 4 H,  $J = 7.8$  Hz, Et  $\text{CH}_2$ ), 0.99 (t, 6 H,  $J = 7.8$  Hz, Et  $\text{CH}_3$ ).

**PhSiMe<sub>2</sub>SiAd<sub>2</sub>CH<sub>2</sub>CHMeCMe=CH<sub>2</sub>:**  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.20–0.45 (m, 8 H, SiCH<sub>2</sub>, SiMe), 0.9 (m, 3 H, Me), 1.35 (s, 3 H, Me), 1.79 (m, 12 H, Ad), 1.85 (m, 6 H, Ad), 1.95 (s, 12 H, Ad), 5.00 (m, 2 H, =CH<sub>2</sub>), 7.2–7.5 (m, 5 H, Ph).

**Photolysis and Thermolysis of 1,1-Diadamantylsiliranes.** **Photolysis.** The reaction mixture was loaded into a quartz sample tube (6 mm (o.d.)  $\times$  4 mm (i.d.)  $\times$  20 cm) connected via a stainless steel sleeve to a Teflon high-vacuum stopcock. After being degassed to 0.02 Torr by freeze-pump-thaw cycles on a vacuum line, the reaction mixture was irradiated with an array of low-pressure mercury lamps in a Rayonet photochemical reactor. After irradiation, the reaction mixture was unloaded in a drybox, and solvent and excess volatile substrates were evaporated under reduced pressure.

**Thermolysis.** The reaction mixture was placed in a Pyrex tube (6 mm (o.d.)  $\times$  4 mm (i.d.)  $\times$  20 cm) with a preformed constriction, attached via a stainless steel adapter to a Teflon high-vacuum stopcock. After being degassed on a vacuum line by freeze-pump-thaw cycles to 0.02

Torr, the sample tube was sealed and then placed in a preheated oil bath. After thermolysis, the sealed tube was opened in a drybox, and solvent and excess volatile substrates were evaporated in vacuo.

The results from both photolysis and pyrolysis experiments, including quantities of reagents, reaction times and temperatures, conversions, product yields, and the isomeric composition of recovered starting and product siliranes are given in Schemes III–V and for competition experiments in Scheme VII.

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**Supplementary Material Available:** Crystal structure drawing, diagram of unit cell, structure determination summary and tables of atomic coordinates, bond lengths, bond angles, anisotropic displacement coefficients, and H atom coordinates (11 pages); observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

## Predominant $^{18}\text{O}$ Exchange Accompanying Base Hydrolysis of a Tertiary Toluamide: *N*-Ethyl-*N*-(trifluoroethyl)toluamide. Assessment of the Factors That Influence Partitioning of Anionic Tetrahedral Intermediates

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**Abstract:** The hydrolysis of *N*-ethyl-*N*-(trifluoroethyl)toluamide (III) in basic media at 100 °C ( $\mu = 1.0$  (KCl)) is reported.  $^{18}\text{O}$  exchange in III recovered from the hydrolytic medium is observed;  $k_{\text{ex}}/k_{\text{hyd}} = 33.4 \pm 1.6$  and is independent of  $[\text{OH}^-]$ . The low basicity of the amine in III ( $\text{p}K_{\text{a}}(\text{H}_2^+\text{N}(\text{Et})\text{CH}_2\text{CF}_3) = 6.3$ ) leads to 2300–3500-fold more exchange in III relative to *N,N*-dimethyltoluamide (I) or *N*-toluoylpyrrolidine (II). These findings indicate that amine leaving ability controls whether a tertiary amide will exhibit  $^{18}\text{O}$  exchange and that restriction of conformational mobility in the manner required by the Deslongchamps' stereoelectronic theory is of little importance in the exchange process. Solvent deuterium kinetic isotope data for III indicate that  $(k_{\text{ex}})_{\text{H/D}} = 0.90 \pm 0.08$  and  $(k_{\text{hyd}})_{\text{H/D}} = 1.05 \pm 0.04$ . These respective solvent kinetic isotope effects (SKIE) refer essentially to isolated kinetic processes  $k_1$  (the attack of  $\text{OH}^-$  to form  $\text{T}_0^-$ ) and  $k_2$  (the breakdown of the anionic intermediate to product). The small observed SKIE on exchange and hydrolysis is analyzed in terms of the fractionation factors for species involved in the transition states leading to the anionic tetrahedral intermediate  $\text{T}_0^-$  and away from it, respectively. The mechanism consistent for the SKIE on  $k_{\text{hyd}}$  is suggested to involve rate-limiting breakdown of one or both of two anionic forms having a protonated N, an anionic zwitterion  $\text{T}_{\text{ZW}}^-$  or a neutral zwitterion with an encounter complex associated  $\text{OH}^-$ . On the basis of SKIE,  $^{18}\text{O}$  exchange, and hydrolysis data for a series of tertiary toluamides having an amine portion varying in basicity by  $\sim 14$  pK units, a unified mechanism for base-promoted hydrolysis is presented.

### Introduction

Carbonyl  $^{18}\text{O}$  exchange has been extensively used to determine the partitioning of anionic intermediates produced during the hydrolysis of amides in base.<sup>1–6</sup> The current scheme that accounts for the observed  $^{18}\text{O}$  exchange is given in eq 1 and involves one or more reversibly formed intermediates (e.g.,  $\text{T}_0^-$ ) in which the  $^{16}\text{O}$  and  $^{18}\text{O}$  atoms are in protonic equilibrium (or near equilibrium).

The order of  $^{18}\text{O}$  exchange for previously investigated benzamides<sup>1,2</sup> and toluamides<sup>6,7</sup> is primary > secondary >> tertiary,

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