Table I. Observed[e] Nitrogen Hyperfine Coupling Constants and g Values for $RCO\dot{N}OC(CH_3)_3$

R	Conditions	a_N, G[f]	g value[g]
Cyclopropyl	*a*	10.50	2.0060
Cyclopropyl	*b*	10.50	2.0060
Cyclopropyl	*c*	10.30	2.0060
Isopropyl	*c*	10.35	2.0058
Phenyl	*c*	10.10	2.0058
p-Methoxyphenyl	*d*	10.20	2.0057
m-Nitrophenyl	*c*	9.60	2.0060
p-Nitrophenyl	*c*	9.60	2.0059
Ethoxy	*c*	11.95	2.0056

[a] Warming **1** in carbon tetrachloride (0.2 *M*). [b] Photolysis of **3** (0.1 *M*) in chloroform at room temperature. [c] Photolysis of di-*tert*-butyl peroxide in *tert*-butyl alcohol (0.1 *M*) in the presence of $RCONHOC(CH_3)_3$. [d] Same as footnote *c* except for the solvent which was $CHCl_3$. [e] Degassing had no important effect other than to sharpen the peaks slightly. [f] Estimated accuracy of ±0.05 G. [g] Relative to DPPH (g = 2.0036) with estimated accuracy of ±0.002.

center where the carbonyl oxygen atom shares some of the spin density. The variations in a_N for the aryl series are in the direction expected of substituent effects. The relative contributions from the dipolar resonance forms, which place a formal negative charge (and no spin) on the nitrogen atom **8b**, should respond to the remote substituents to produce this pattern.

INDO[6] calculations, for the *N*-hydroxyformamido species with the structure shown, **9**, give an unprojected nitrogen hyperfine coupling constant of 9.5 G in good agreement with the observed values. Calculations were carried out on a number of other nuclear structures;[7] all were predicted to be of higher energy and none predicted hyperfine coupling constants close to those observed here.[8]

We believe these observations strongly support the conclusion that these *N*-alkoxyamido radicals are π radicals. They also provide direct support for the suggestions made previously by Cooley[2] and his coworkers concerning possible mechanisms of denitrosation and ester formation from nitrosohydroxamates. The denitrosation process becomes an important contributor for **1** because of its slow rate of rearrangement (less than one-tenth that of the benzoyl compound). Such processes contribute to a much smaller extent with aryl or acyclic secondary alkyl side chains.

Acknowledgment. We are grateful to the National Science Foundation and the E. I. du Pont Co. for financial support of this work. We are also grateful to Professor C. E. Klopfenstein for assistance with the adaptation of the INDO computer program to our system.

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(6) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, 90, 4201 (1968).

(7) The INDO calculations were not minimized with respect to geometry. The assumed bond lengths and bond angles were taken from "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, 1965, or from ref 5.

(8) Professor W. Danen has privately communicated to us that his group has observed the esr spectrum of the *N*-*tert*-butoxypropionamido radical in *tert*-butyl alcohol. The observed a_N was 10.98. The reasons for the discrepancy in a_N between their laboratories and ours are not apparent at the present time.

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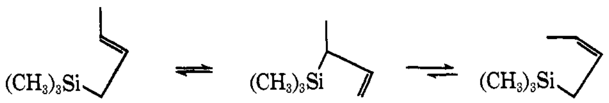
Unimolecular Thermal Rearrangement of Allylsilanes. A Sigmatropic 1,3 Migration of Silicon

Sir:

The thermal thiallylic rearrangement of allyl phenyl sulfides has been reported[1] to occur both unimolecularly and bimolecularly *via* a well-defined reaction intermediate involving development of negative charge on sulfur and positive charge on the β carbon of its allyl substituent. Such an intermediate could arise through utilization of a 3d orbital of the sulfur, or alternatively a three-center four-electron bonded structure[2] or what has been designated as a hypervalent structure.[3] It seemed appropriate, therefore, to inquire into the possibility that the periodic system neighbors of sulfur could also employ analogous reaction pathways.

A thermally induced 1,5 rearrangement of silicon has been discovered[4] but no established example of an uncatalyzed, thermal 1,3 silallylic rearrangement exists in the literature. On the other hand, carbon, which has no "available" d orbitals, has been reported[5] to undergo both 1,3 and 1,5 sigmatropic changes. The missing 1,3 rearrangement mode in silicon has now been identified and characterized as one of common occurrence *via* a relatively low-energy route, when allylsilanes are heated (either) to *ca.* 500° in the gas phase[5] for very short reaction times, or to *ca.* 275° in the liquid phase[5] for somewhat longer periods. The kinetic factors controlling the course of this reaction and their mechanistic implications are considered in the following preliminary account of the studies conducted.

Heating α-methylallyltrimethylsilane (**1**) for less than 1 min at about 500° in a helium stream converted it to a mixture consisting mostly of the γ (crotyl) isomer, whose composition was not altered significantly on prolonged heating. When the pure *trans*-crotyltrimethylsilane (**1a**) was thermolyzed under similar conditions, the same "equilibrium" composition (*ca.* 5:95) of α and γ isomers was quickly realized, but continued heating resulted in a gradual increase of **1b**, the *cis*-crotyl. Moreover, heating the pure *cis*-crotyl **1b** produced the same "equilibrium" concentration of the α-isomer **1** and a gradual increase of the *trans*-crotyl component **1a**, all of which suggested the scheme



1a (trans) 34% **1** 5% **1b** (cis) 61%

The kinetics of the rearrangement were studied in the gas phase in a flow system utilizing a gold coil reactor known[6] to entail only negligible wall effects. The reac-

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(1) H. Kwart and N. Johnson, *J. Amer. Chem. Soc.*, **92**, 6064 (1970).

(2) E. E. Havinga and E. H. Wiebinga, *Recl. Trav. Chem. Pays-Bas*, **78**, 724 (1959).

(3) J. I. Musher, *J. Amer. Chem. Soc.*, 90, 7371 (1968); *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969); "Conformational Analyses," G. Chiurdoglu, Ed., Academic Press, New York, N. Y., 1971, p 177.

(4) H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.*, **4**, 313 (1965); A. Davison and P. E. Rakita, *Inorg. Chem.*, **9**, 289 (1970); A. J. Ashe III, *Tetrahedron Lett.*, 2105 (1970).

(5) See, for examples: (i) J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **89**, 5305 (1967); (ii) J. A. Berson, *Accounts Chem. Res.*, 1, 152 (1968); and (iii) R. B. Woodward and R. Hoffmann, "Conservation of Orbital Symmetry," Verlag Chemie GmbH–Academic Press, Weinheim/Bergstr., Germany, 1970.

(6) H. Kwart, S. F. Sarner, and J. H. Olson, *J. Phys. Chem.*, **73**, 4056 (1969).

Table I. Reaction Parameters of Gas-Phase 1,3-Silyl Rearrangements

Substrate	Silane	Temp range, C°	C_e %[a]	E_a, kcal/mol[b]	Log A	$\Delta S^{\ddagger}$, eu[c]	Product, % cis	Compd, % trans
Trimethyl-α-methylallyl	**1**	506–567	5.4	47.7 ± 0.3	$12.3_2 \pm 0.07$	−6.2 ± 0.3	64	36
Dimethylphenyl-α-methylallyl	**2**	500–572	5.5	47.2 ± 0.2	$12.1_9 \pm 0.06$	−6.8 ± 0.3	60	40
Dimethylphenyl-α,β-dimethylallyl	**3**	516–577	5.3	47.7 ± 0.3	$12.2_6 \pm 0.07$	−6.6 ± 0.3	50	50
Trimethyl-α-phenylallyl	**4**	420–480	1.9	42.5 ± 0.2	$11.9_7 \pm 0.07$	−7.4 ± 0.3	41	59

[a] Per cent unrearranged starting material at equilibrium, the specific rate constant for disappearance of starting material being calculated; $k = -\log[(C - C_e)/(C_0 - C_e)]/t$. [b] E_a was calculated by linear regression analysis of the plot of log k *vs.* $10^3/T$. A minimum of 20 experimental determinations of k was encompassed in this analysis. [c] The entropy of activation at 500° (calculated in the usual way from E_a and log A).

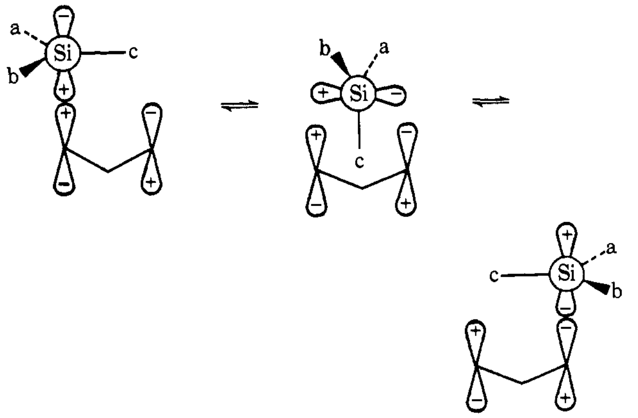
tion was unimolecular up to (at least) 90% rearrangement. Analysis of the rate data yielded $E_a = 47.7$ kcal/mol and $\Delta S^{\ddagger} = -6.2$ eu at 500° (see Table I). The negative activation entropy suggested a cyclic concerted transition state, as opposed to a radical dissociation mechanism previously[4] considered for other thermolysis reactions of the allylsilanes. Furthermore, the absence of cross-products,[1] when two differently substituted allylic silanes were cothermolyzed, provides additional support for the intramolecular process of rearrangement. It is also to be noted that the activation energy determined is considerably below the bond dissociation energy of Si–C even allowing for allylic stabilization of the carbon radical.

A series (**2**–**4**) of substituted allylic silanes was prepared and subjected to kinetic studies in an effort to distinguish between the various mechanistic courses by which the rearrangement could occur. The results summarized in Table I provide convincing evidence for a symmetrical transition state of sigmatropic migration of silicon. Thus, substitution of a phenyl for methyl on the silicon has no appreciable effect on the activation parameters. A homolytic or heterolytic mechanism of rearrangement would demand a very considerable response of rate to such a wide variation in the nature of substituents bonded to the migrating atom. Moreover, the formation of an intermediate of the type suggested by the results obtained in thermal rearrangement of allylic sulfides[1] is also ruled out. The complete lack of charge or radical development on silicon during the course of rearrangement, such as has been identified in the sulfur rearrangement process,[1] is also confirmed by the total absence (see Table I) of any rate or activation effects resulting from substitution of methyl at the β carbon (in **3**).

The only substituent influences on the rates and activation parameters (to be perceived in the reaction series studied) are those anticipated on the basis of prior results and considerations in well-established concerted rearrangement processes.[7] Thus, in the absence of significant steric factors, in cases where substitution results in a large degree of stabilization of the product relative to the reactant, the symmetrical transition state reflects this factor in a lowering of E_a without influencing the sign or magnitude of $\Delta S^{\ddagger}$, while shifting the equilibrium composition in favor of the product. This effect is clearly a rate-controlling factor in the case of **4**, the α-phenylallyltrimethylsilane rearrangement to the γ isomer. Here conjugation of the aromatic ring with the allylic double bond has decreased E_a by more than 5 kcal, with very little change in $\Delta S^{\ddagger}$, while the amount of unrearranged (α) isomer at equilibrium has declined to less than 2%.

A final point for comment is related to the observed cis/trans product ratios. Since the silyl group can migrate either above or below the plane of the allyl framework (in the HOMO) one might have expected a 50:50 cis–trans mixture of γ isomers. Reference to Table I indicates that although the product compositions in all instances studied are not far from 50:50, conformational factors arising from eclipsing and other nonbonded interactions in the transition states can result in some preference for forming one of the alternative configurations of the product.

On the basis of orbital symmetry considerations, a suprafacial 1,3 sigmatropic rearrangement involving an antisymmetric 3p silicon orbital is expected to occur with inversion of configuration (as illustrated below).



Experiments to test this hypothesis have been initiated. These results will be discussed together with the full details of the current work in a future article.

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(7) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).

Acyl and Alkyl Tetracarbonylferrate(0) Complexes as Intermediates in the Synthesis of Aldehydes and Ketones

Sir:

Disodium tetracarbonylferrate(−II) is an inexpensive, selective reagent for the high yield conversion of aliphatic halides and tosylates into aldehydes and unsymmetrical ketones.[1,2] Earlier we proposed that alkyl and

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(1) M. P. Cooke, *J. Amer. Chem. Soc.*, **92**, 6080 (1970).

(2) J. P. Collman, S. R. Winter, and D. R. Clark, *ibid.*, submitted for publication.