$MgBr_2$, the experiments involving a large excess of product, ROMgBr, with the resolution of k_4 and k_5, the independence of the total rate behavior on initial Grignard reagent concentration at constant excess ketone concentration, and the association data. Nowhere are additional parameters, *e.g.*, salt effects, required to fit the data to a particular mechanism. All conclusions are drawn from fundamental values, *i.e.*, measured equilibrium constants and measured rates.

It should be emphasized that all of the steps represented by eq 21–27 are important in describing the reaction of methylmagnesium bromide with excess 2-methylbenzophenone. The same mechanistic steps hold for the reaction in excess Grignard reagent except that the steps after eq 21 become relatively unimportant. This is due to the fact that the concentrations and reactivity of $ROMgCH_3$, $G \cdot P$, and $G \cdot P_2$ are relatively low compared to $(CH_3)_2Mg$ and CH_3MgBr and, therefore, the reaction proceeds mainly by the sequence described by eq 21. When the Grignard to ketone ratio is the same or nearly the same, it is clear that the steps described by eq 22–27 once again become important.

Chemistry of Atomic Silicon. III. Reactions of Electron Bombardment Produced Silicon Vapor with Silanes

Philip S. Skell* and Peter W. Owen

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received December 9, 1971*

Abstract: Silicon atoms were found to react with trimethylsilane, dimethylsilane, methylsilane, and disilane exclusively by insertion into silicon–hydrogen bonds. The resulting silenes inserted into a silicon–hydrogen bond of another substrate molecule, or polymerized to form linear and cyclic polysilanes. The electron bombardment of solid-phase silanes at 77°K gave products derived from silene intermediates.

The fact that compounds containing silicon–hydrogen bonds are notably good trapping agents for carbenes,[1] carbon atoms,[2] and silenes[3] made this class of substrates a logical choice for a study of silicon atom reactions. The cocondensation of thermally produced silicon vapor with trimethylsilane has previously been reported.[4] Reactions of recoil silicon atoms produced by the nuclear transformation $^{31}P(n,p)^{31}Si$ with silane[5,6] and by the transformation $^{30}Si(n,\gamma)^{31}Si$ with silane[7] and with silane, disilane, and trisilane[8] have also been reported.

Experimental Section

The apparatus and procedure used was basically the same as that described for the study of carbon atom reactions.[9] Reactions were carried out by simultaneously depositing silicon vapor and a large excess of substrate on the liquid nitrogen cooled walls of an evacuated ($<1 \times 10^{-4}$ Torr) reaction flask. Silicon vapor was produced by electron bombardment heating of a silicon electrode to its melting point using a Varian 4000-V electron gun. Gaseous substrates were introduced into the system by means of a perforated glass inlet bulb, designed to produce an even layer of coverage in the zone of silicon deposition. Reactions occurred in the condensed phase at the walls of the system, either at ~77°K, or upon warm-up.

In a typical reaction, 20–30 mg of silicon and ~10 g of substrat were continuously deposited over a period of about 1 hr. The reaction flask was then warmed to room temperature and the volatile contents were transferred to a standard vacuum line for work-up. Noncondensible gases produced both during the codeposition and during warm-up were collected *via* a Toeppler pump and analyzed by vpc. Products were separated by trap to trap fractionations and vapor-phase chromatography, and identified by comparison of their infrared, nmr, and mass spectra with authentic samples or with literature spectra. The identification of products for which no spectra could be found in the literature are presented below.

Blank reactions were run by depositing the substrates on the flask walls with the electron gun turned on, but with no silicon source material present. The reaction and work-up conditions of the corresponding reactions were duplicated as closely as possible in the blanks.

Yields of silicon atom products reported were based on millimoles of product divided by millimoles of silicon vapor reaching the walls of the system.

Trimethylsilane was purchased from Peninsular Chemical Research and used without further purification. Dimethylsilane and methylsilane were synthesized by the reduction of dimethyldichlorosilane and methyldichlorosilane, respectively, with lithium aluminum hydride. Disilane was synthesized by the lithium aluminum hydride reduction of hexachlorodisilane.

Identification of Products. 1,1,3,3-Tetramethyltrisilane was identified by its 70-eV mass spectrum (parent ion at *m/e* 148 (6.7%), base peak at *m/e* 88), vapor infrared spectrum (10-mm cell; C–H (3000 cm^{-1}), SiH (~2120 cm^{-1}), Si–CH_3 (~1255 cm^{-1}), no absorptions in the Si–O or $SiCH_2Si$ regions (1200–950 cm^{-1})), and nmr spectrum in benzene (Table I).

Table I. The 60-Mc Nmr Spectrum of 1,1,3,3-Tetramethylsilane

Resonance	Chemical shift,[a] τ	Rel area	*J*, cps
$-CH_3$ (doublet)	9.73	6.17	~4
$-Me_2Si-H$ (multiplet)	5.87	1.03	
$-SiH_2-$ (triplet)	6.02	1.00	~4

[a] Referred to the benzene solvent absorption at τ 2.72.

---

[1] C. J. Mazac and J. W. Simons, *J. Amer. Chem. Soc.*, **90**, 2484 (1968).

[2] P. S. Skell and P. W. Owen, **94**, 1578 (1972).

[3] W. H. Atwell and D. R. Weyenberg, *Angew. Chem., Int. Ed. Engl.*, 8, 469 (1969).

[4] P. S. Skell and P. W. Owen, *J. Amer. Chem. Soc.*, 89, 3933 (1967).

[5] P. P. Gaspar, B. D. Pate, and W. Eckelman, *ibid.*, 88, 3878 (1966).

[6] P. P. Gaspar, S. A. Bock, and W. C. Eckelman, *ibid.*, **90**, 25, 6914 (1968).

[7] P. P. Gaspar, S. A. Bock, and C. A. Levy, *Chem. Commun.*, 1317 (1968).

[8] G. Cetini, M. Castiglioni, P. Volpe, and O. Gambrino, *Ric. Sci.*, **39**, 392 (1969).

[9] P. S. Skell, L. D. Wescott, Jr., J. P. Goldstein, and R. R. Engel, *J. Amer. Chem. Soc.*, 87, 2829 (1965).

1,3-Dimethyltrisilane was identified by its mass spectrum (12 eV, parent ion at *m/e* 120 (23%), base peak at *m/e* 74), vapor infrared spectrum (12 mm, C–H (3.37 μ), SiH (4.69, 4.72 μ), Si–CH_3 (7.94 μ), no absorptions in the region characteristic of SiO or Si–CH_2–Si groups (8–10 μ)), and nmr spectrum in benzene (see Table II). A vapor uv spectrum (100-mm cell) showed no absorption maximas in the region 200–350 mμ.

Table II. The 60-Mc Nmr Spectrum of 1,3-Dimethyltrisilane

Resonance	Chemical shift[a], τ	Rel area	*J*, cps
–CH_3 (triplet)	9.83	3.18	~5
–SiH_2– (quintet)	6.80	1.00	~3.5
CH_3–SiH_2– (multiplet)	6.10	1.95	

[a] Referred to the benzene solvent at τ 2.72.

n-Pentasilane was identified from its mass spectrum (14 eV, parent peak at *m/e* 152 (3.7%), base peak at *m/e* 120), infrared spectrum, and nmr spectrum. The relative order of intensity of the peak envelopes for the five different types of ions in the mass spectrum was $Si_4^+ > Si_3^+ > Si_2^+ > Si_5^+ > Si_1^+$. A similar relative order of intensities ($Si_3^+ > Si_2^+ > Si_4^+ > Si_1^+$) has been reported for the mass spectrum of *n*-Si_4H_{10}.[10] The vapor infrared spectrum was strikingly similar to that of an authentic sample of *n*-Si_4H_{10}, except that the absorptions in the region 800–600 cm^{-1} were shifted to lower frequency, falling at ~740 (w), 730 (m), 701 (w), 681 (s), 646 (s), and 632 cm^{-1} (shoulder).

The nmr spectrum was taken of a vpc purified sample in benzene in a sealed, evacuated nmr tube. The main resonance was centered at τ ~3.46, and was very complicated due to the similarity in the chemical shift differences and coupling constants of SiH_3 and SiH_2 protons. The ^{29}Si satellite absorptions served to unambiguously identify the compound as the n isomer. The spectrum is summarized in Table III.

Table III. Chemical Shifts and Coupling Constants in the 100-Mc Nmr Spectrum of *n*-Pentasilane

Group	Chemical shift,[a] ppm	Group	*J*, cps
–SiH_3	3.46	–$^{29}SiH_3$	199
SiH_3–SiH_2	3.33	SiH_3–^{29}*SiH*$_2$	194
–SiH_2)$_2$–SiH_2	Unknown (~3.33)	SiH_3SiH_2–^{29}*SiH*$_2$	Unknown
		SiH_3–SiH_2–	3.5
		–SiH_2–SiH_2–	Unknown

[a] Chemical shifts parts per million to low field of TMS.

Results

A. Reaction of Silicon Vapor with Trimethylsilane. The reaction of thermally vaporized silicon and trimethylsilane produced 1,1,1,3,3,3-hexamethyltrisilane in 27% yield along with a nonvolatile residue. Small quantities of hexamethyldisilane and hexamethyldisiloxane were observed by retention time.

The reaction of electron-bombardment-produced silicon vapor with trimethylsilane also produced 1,1,1,-3,3,3-hexamethyltrisilane (14%) and a nonvolatile residue. Approximately ten other minor products were formed which were also formed in the blank reaction. The two largest of these were hexamethyldisilane and hexamethyldisiloxane.

B. Reaction of Silicon Vapor with Dimethylsilane. The products from a reaction of electron-bombardment produced silicon vapor (60.4 mg, 2.14 mmol) and dimethylsilane (9.5 g) and from the disilane blank are presented in Table IV.

Table IV. Products from the Dimethylsilane Reaction and Blank

Product	Reaction, mmol	Blank, mmol
H_2	0.419	0.296
CH_4	0.105	0.087
C_2H_6	0.001	Unknown
1,1-$(CH_3)_2Si_2H_4$	0.011	0.007
1,1,2-$(CH_3)_3Si_2H_3$	0.049	0.056
1,1,3,3-$(CH_3)_4Si_3H_4$	0.637	0.000
Residue	~0.1–0.2 g	~10 mg

1,1,3,3-Tetramethyltrisilane (30% yield) and nonvolatile residue were the only products obtained from dimethylsilane that were due to reactions of vaporized silicon atoms.

C. Reaction of Silicon Vapor with Methylsilane. The products formed from the reaction of electron-bombardment-produced silicon vapor (19.9 mg, 0.705 mmol) and methylsilane (9 g), and from the methylsilane blank are presented in Table V.

Table V. Products from the Methylsilane Reaction and Blank

Product	Reaction, mmol	Blank, mmol
H_2	1.629	1.233
CH_4	0.173	0.144
$CH_3SiH_2SiH_3$	0.066	0.063
1,2-$(CH_3)_2Si_2H_4$	0.357	0.334
1,3-$(CH_3)_2Si_3H_6$	0.238	0.000
1,2,3-$(CH_3)_3Si_3H_5$	0.050	0.068
$(CH_3)_2Si_4H_6$	0.009	0.000
Residue	~100 mg	~10 mg

Two of the products listed in Table V are implicated as silicon atom products: 1,3-dimethyltrisilane in 34% yield, and $(CH_3)_2Si_4H_6$ in ~2.5% yield (after correcting for two vaporized silicon atoms per molecule of product). In addition to these, much of the nonvolatile residue obtained must have contained vaporized silicon atom products.

The structure of the product $(CH_3)_2Si_4H_6$ was not fully determined. A 70-eV mass spectrum showed a parent peak at *m/e* 148 which was also the largest peak in the spectrum. Computer measurement of the *m/e* 148 isotope peak areas indicated the relative isotope distribution P = 100%, P + 1 = 23.2%, P + 2 = 15.9%, and P + 3 = 2.6%, in excellent agreement with the ratio calculated for the empirical formula $Si_4C_2H_{12}$ of P = 100.0%, P + 1 = 22.9%, P + 2 = 15.6%, and P + 3 = 2.8%.

An infrared spectrum showed a strong SiH stretch (4.70 μ), a weak CH stretch (3.36, 3.44 μ), and an absorption at 8.0 μ for Si–CH_3 groups. No absorptions were present in the SiO or $SiCH_2Si$ regions, nor were any absorptions characteristic of carbon–carbon double bonds observed. It was concluded that both carbons must be present as methyl groups.

An nmr spectrum showed three regions of absorption at τ 9.4–9.9, ~6.6, and ~6.0 of relative area 6.0 : 2.0 : 3.6, respectively. Spin decoupling experiments showed that the methyl region (τ 9.4–9.9) and the region at τ 6.0 were coupled. The complexity of the methyl region in-

---

(10) S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, 3, 946 (1964).

dicated the material collected was a mixture of two isomers. It is considered most likely that these compounds were methyl-substituted cyclotetrasilanes.

D. Reaction of Silicon Vapor with Disilane. The products from the reaction of electron-bombardment-produced silicon vapor (24.8 mg, 0.880 mmol) and disilane (2.4 g), and from the disilane blank are presented in Table VI.

Table VI. Products from the Disilane Reaction and Blank

Product	Reaction, mmol	Blank, mmol
H_2	1.231	0.687
SiH_4	0.785	0.707
Si_3H_8	0.678	0.251 (?)
n-Si_4H_{10}	0.181	0.129
Si_5H_{12}	0.010	0.001
n-Si_5H_{12}	0.158	0.000
Si_5H_{10}	0.017	0.005
Si_5H_{10}	0.009	0.002
Residue	>100 mg	~10 mg

n-Pentasilane (18% yield) and nonvolatile residue are the only products observed that were due to reactions of vaporized silicon atoms. From Table VI, comparison of the amounts of Si_3H_8 produced in the silicon vapor reaction and the blank would lead one to believe Si_3H_8 was also a silicon atom product from disilane. However, we believe the Si_3H_8 result obtained in the blank was in error, for in another disilane reaction (with 4.45 mmol of silicon vapor) and its corresponding blank, the SiH_4/Si_3H_8 mol ratios were essentially the same, indicating that Si_3H_8 was derived from substrate decomposition rather than silicon atom reactions.

Both of the Si_5H_{10} isomers showed parent peaks at m/e 150 in their low eV mass spectra, no infrared absorptions in the SiO or C–H regions, and weak absorptions in the region from 205 to 215 mμ in their vapor ultraviolet spectra. Quantities sufficient for nmr spectra were not isolated.

Discussion

A. Silicon Atom Reactions. Silicon atoms reacted with substrates examined in this work by insertion into silicon–hydrogen bonds to form silenes.

$$:\!Si\!: + R_3SiH \longrightarrow R_3Si\text{-}\underset{\cdot\cdot}{Si}\text{-}H$$

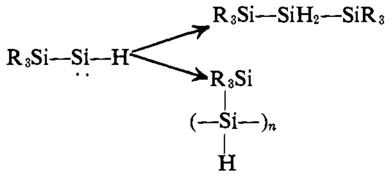
$$(R = CH_3, H, SiH_3)$$

No products were isolated that indicated carbon–hydrogen,[11] carbon–silicon,[12] or silicon–silicon[13] bond insertion had occurred. The silene intermediates thus genhratec reacted to form stable products by (a) insertion into a silicon–hydrogen bond of another substrate molecule or (b) polymerization to form polysilanes. The yields of diinsertion products are summarized in Table VII.

Table VII. Diinsertion Products Isolated from Silicon Vapor and Silane Substrates

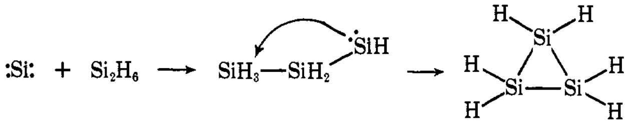
Substrate	Product	% yield	Rel reactivity per Si–H bond
Me_3SiH^a	$Me_3Si{-}\mathit{Si}H_2{-}SiMe_3$	27	27
Me_3SiH^b	$Me_3Si{-}\mathit{Si}H_2{-}SiMe_3$	14	14
$Me_2SiH_2{}^b$	$Me_2SiH{-}\mathit{Si}H_2{-}SiHMe_2$	30	15
$MeSiH_3{}^b$	$MeSiH_2{-}\mathit{Si}H_2{-}SiH_2{-}Me$	34	11
$H_3SiSiH_3{}^b$	$SiH_3SiH_2{-}\mathit{Si}H_2{-}SiH_2SiH_3$	18	3

[a] Silicon vapor produced by resistive heating. [b] Silicon vapor produced by electron bombardment.



Evidence for the electrophilic character of SiH_2 has been presented.[14] From Table VII, a comparison of the relative reactivities of the silane substrates per silicon–hydrogen bond suggests that the silylsilenes formed in this work also exhibited electrophilic character, favoring insertion into substrates having increasing methyl substitution.

The reaction of silicon vapor with disilane was examined carefully for the presence of trisilacyclopropane. Such a product might logically be expected to be formed through an intramolecular diinsertion.



Although monosilacyclopropanes have been shown to be thermally unstable reaction intermediates, rearranging to vinylsilanes, it was reasoned that di- and trisilacyclopropanes might be isolable since there is no comparable rearrangement product which would be stable because it would require a double bond to silicon. The gentle conditions under which reactions are run and worked up in this study (low temperature and under vacuum) should have optimized the possibility for the observation of such a product. This compound was not observed in the product mixture (all chromatographic peaks of retention time equal to or less than that of *n*-pentasilane were identified). The failure to isolate a trisilacyclopropane from double insertion of a silicon atom into disilane suggests that either $SiH_3SiH_2\ddot{Si}H$ did not have an opportunity to cyclize, or the trisilacyclopropane dissociated into a diradical.

Vpc–mass spectral analysis of the high boiling products in the residue from the methylsilane reaction showed groups of products having a progression of molecular weights of 134, 148, 162, 176, 178, 192, and higher. Assuming the products contained only carbon, hydrogen, and silicon, and that the highest mass peak in each spectrum was the molecular ion, most of these masses require structures that have one degree of unsaturation. These molecular weights were also sums of whole number multiples of the masses 74, 44, and 30, the molecular weights of silenes $CH_3SiH_2\ddot{Si}H$, $CH_3\ddot{Si}H$, and $:\!SiH_2$. The former was derived from insertion of a silicon atom into the silicon–hydrogen

---

[11] Had C–H bond insertion occurred, products containing Si–CH_2–Si linkages would have resulted.

[12] Had Si–C bond insertion occurred, products containing methyl groups on all three silicons in the diinsertion product fraction would have resulted.

[13] Had Si–Si bond insertion occurred, isopenta- and neopentasilane should have been recovered.

[14] P. Estacio, M. D. Sefcik, E. K. Chan, and M. A. Ring, *Inorg. Chem.*, **9**, 1068 (1970).

bond of methylsilane, and the latter from electron bombardment of methylsilane forming the silenes and hydrogen or methane. This suggests that these higher products were polymerization products of the three silenes present in the matrix. The observation that most of these products appear to have structures Si_nR_{2n} (R = H and CH_3) rather than Si_nR_{2n+2} suggests that the polymer chains were usually terminated by cyclization, and only to a minor extent by radical abstraction.

B. Electron Bombardment Decomposition of Silanes. The use of electron bombardment heating in silicon vapor reactions always resulted in some decomposition of the substrates. Experiments in which the conditions of light and heat emitted from the electron gun were approximately duplicated, but the high potential drop across the electron gun was removed so that no electron beam was generated, showed that substrate decomposition was not a result of thermolytic or photolytic processes. Instead, it is felt the decomposition products were caused by electron bombardment of the solid-phase substrate near 77°K by stray electrons.

The largest decomposition product formed by the electron bombardment of trimethylsilane was hexamethyldisilane. This is in keeping with dissociation of the substrate to form trimethylsilyl radicals. It is in agreement with the primary mode of decomposition upon pyrolysis.[15]

$$Me_3SiH \xrightarrow{e} Me_3Si\cdot + H\cdot \longrightarrow Me_3SiSiMe_3 + H_2$$

The electron bombardment decomposition of dimethylsilane produced a spectrum of products which were in accord with decomposition by elimination of silenes.

$$\begin{aligned} Me_2SiH_2 \xrightarrow{e} {} & Me_2Si\colon + H_2 \\ & Me(H)Si\colon + CH_4 \\ & H_2Si\colon + C_2H_5 \end{aligned}$$

These inserted into silicon–hydrogen bonds of undecomposed dimethylsilane to form the observed disilanes, or polymerized to form higher polysilanes.

$$\begin{aligned} Me_2Si\colon + Me_2SiH_2 &\longrightarrow Me_2SiH\text{–}SiHMe_2 \\ Me(H)Si\colon + Me_2SiH_2 &\longrightarrow MeSiH_2\text{–}SiHMe_2 \\ H_2Si\colon + Me_2SiH_2 &\longrightarrow SiH_3\text{–}SiHMe_2 \end{aligned}$$

The absence of 1,2-dimethyldisilane and the presence of 1,1-dimethyldisilane both suggest that silene intermediates were involved in the decomposition reaction rather than monoradical intermediates.

Decompositions of methylsilane by pyrolysis,[16] silent electric discharge,[17] and direct vacuum uv and Xe-sensitized photolysis[18] have all been rationalized in terms of silene intermediates. The silenes reacted by insertion into the Si-H bonds of undecomposed starting material, and, in some cases, added silanes.

From electron bombardment of methylsilane, methyldisilane and 1,2-dimethyldisilane were formed.

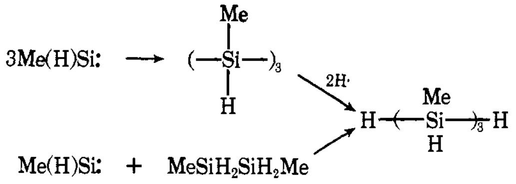
$$MeSiH_3 \xrightarrow{e} Me(H)Si\colon + H_2$$

$$MeSiH_3 \xrightarrow{e} H_2Si\colon + CH_4$$

$$MeSiH_3 + Me(H)Si\colon \longrightarrow MeSiH_2SiH_2Me$$

$$MeSiH_3 + H_2Si\colon \longrightarrow MeSiH_2SiH_3$$

Another product, 1,2,3-trimethyltrisilane, may have been formed by two processes



Disilane and ethane, products that would be expected from a monoradical process, were not observed, although this may have been because of the difficulty in separating small quantities of these products from the excess methylsilane present. The silene mechanism is favored in this case because of the similarity of the product distribution to that obtained from pyrolysis and vacuum uv photolysis of methylsilane. The products observed from triplet mercury sensitized photolysis of methylsilane (which was shown to proceed by a radical mechanism)[19] did not include methyldisilane.

The electron bombardment decomposition of disilane produced hydrogen, silane, trisilane, *n*-tetrasilane, and higher polysilanes. Pyrolysis of disilane has previously been reported to proceed by elimination of SiH_2, which then inserts into disilane to produce trisilane.[20] Some *n*- and *i*-tetrasilane was also produced by the secondary process

$$\colon SiH_2 + Si_3H_8 \longrightarrow n\text{- and } i\text{-}Si_4H_{10}$$

It seems unreasonable to attribute the presence of tetrasilane to $:SiH_2$ insertion into trisilane in this study. The reactions were carried out in high dilution in excess disilane, minimizing collisions between products and reactive intermediates. Furthermore, it was clearly found that only *n*-tetrasilane was produced and that no *i*-tetrasilane was present.

The products may be explained either by the intermediacy of silyl and disilyl radicals, or *via* the formation of silene and silylsilene. Of these two possible routes, the latter is considered more likely. Large quantities of polymeric silanes having five or more silicons per molecule would not be expected from a monoradical process, and are more in keeping with the polymerization of silene intermediates. The postulated mechanism for the decomposition is as follows:

$$Si_2H_6 \xrightarrow{e} \colon SiH_2 + SiH_4$$

$$Si_2H_6 \xrightarrow{e} \colon SiH\text{–}SiH_3 + H_2$$

$$\colon SiH_2 + Si_2H_6 \longrightarrow Si_3H_8$$

$$\colon SiHSiH_3 + Si_2H_6 \longrightarrow n\text{-}Si_4H_{10}$$

$$n\colon SiH_2 + n\colon SiHSiH_3 \longrightarrow \text{polymer}$$

It is interesting to note that despite the fact that silenes were generated (either by silicon atom insertion or by substrate decomposition) in high dilution in this study, a significant fraction of the intermediates survived enough collisions with substrate molecules to polymerize. It must be concluded that the silene inter-

---

[15] J. Binenboym and R. Schaeffer, *Inorg. Chem.*, 9, 1581 (1970).

[16] J. J. Kohanek, P. Estacio, and M. A. Ring, *ibid.*, 8, 2516 (1969).

[17] E. A. Groschwitz, W. M. Ingle, and M. A. Ring, *J. Organometal. Chem.*, 9, 421 (1967).

[18] O. P. Strausz, E. Jakubowski, H. S. Sundu, and H. E. Gunning, *J. Chem. Phys.*, 51, 522 (1966).

[19] M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, 87, 179 (1965).

[20] E. M. Tebben and M. A. Ring, *Inorg. Chem.*, 8, 1787 (1969).

mediates were reasonably stable at liquid nitrogen temperature.

The distribution of molecular weights of the polymeric products was striking in that only higher molecular weight silene self-condensation products were formed. Lower molecular weight species, *i.e.*, dimers and trimers resulting from the condensation of only two or three silene units, were not observed. Normally, one would expect to find a continuous distribution of chain lengths, so that the observation of a large yield of monomeric silene products should be accompanied by large amounts of dimer and trimer. The absence of these lower molecular weight polymeric species suggests that the intermediates involved are considerably less reactive than the silene intermediates responsible for the formation of monomeric products.

It is reasonable to assume that polymerization of silenes occurred in our system in the fashion described by Margrave and Wilson for the condensation of singlet SiF_2 to form triplet diradicals.[21]

$$\uparrow\downarrow\dot{\mathrm{Si}}\mathrm{F}_2 \xrightarrow{\mathrm{SiF}_2} \uparrow\dot{\mathrm{Si}}\mathrm{F}_2\dot{\mathrm{Si}}\mathrm{F}_2\uparrow \xrightarrow{\mathrm{SiF}_2} \uparrow\dot{\mathrm{Si}}\mathrm{F}_2\mathrm{SiF}_2\dot{\mathrm{Si}}\mathrm{F}_2\uparrow \xrightarrow{\mathrm{SiF}_2} \text{etc.}$$

If the silene intermediates responsible for the formation of monomeric silicon atom products were also in the triplet state, one would expect them to be of approximately the same reactivity as the triplet diradicals formed in the polymerization process. The great difference in reactivity observed thus leads us to believe the monomeric products must have had a singlet state silene precursor.

Acknowledgment. We gratefully acknowledge the financial support of the Air Force Office of Scientific Research.

---

[21] J. L. Margrave and P. W. Wilson, *Accounts Chem. Res.*, 4, 145 (1971).

Stereochemistry of Sulfur Compounds. III. Radical-Chain Mechanism for Racemization of Sulfinamides[1,2]

Robert E. Booms and Donald J. Cram*

Contribution No. 2901 from the Department of Chemistry of the University of California at Los Angeles, Los Angeles, California 90024.
Received September 29, 1971

Abstract: Optically pure (+)-*N*-phenyl-*p*-toluenesulfinamide ((+)-**1**), (+)-*N*-(α-naphthyl)-α-naphthalenesulfinamide ((+)-**2**), and (−)-*N*-methyl-*N*-phenyl-*p*-toluenesulfinamide ((−)-**3**) racemized at 25° in neutral, purified, deoxygenated benzene, and (−)-**3** at 25° in deoxygenated, purified hexamethylphosphoramide. The reactions exhibited radical-chain behavior characterized by varying induction periods, pseudo-first-order kinetics, and inhibition by di-*tert*-butyl nitroxide. That scission of the S–N bond was involved in racemization was demonstrated through crossbreeding of the nitrogen and sulfur parts of **1** and **2** to give 46% disproportionation products. Compound **3** inefficiently initiated styrene and methyl methacrylate polymerization at 25°. The mechanism consistent with these facts is one initiated by homolysis of the S–N bond, followed by a chain-radical displacement reaction of N· by N· on S.

In recent years different mechanisms of racemization at chiral sulfur centers in the *sulfin* oxidation state have been reported.[3–5] Sulfoxides have been racemized photochemically,[3a] by thermally induced homolytic cleavage and recombination,[3b] by reversible allylic rearrangement through allyl sulfenate esters,[3b,c] by reversible nucleophilic substitution at sulfur with nucleophilic acids,[3d] and by pyramidal inversion at high temperatures.[3b] The lowest energy pathway varied greatly with structure and catalyst. Sulfonium salts[4a] and sulfonium ylides[4b] racemized by simple pyramidal inversion at 25–50°. Alkyl sulfinate esters were shown to racemize and rearrange to sulfones in acetic acid through an ion-pair intermediate,[5b] and thiosulfinates racemized by an internal ligand-exchange mechanism involving an achiral point on the reaction coordinate.[5a]

From the variety of racemization mechanisms observed, the generalization emerges that chiral sulfur centers in the *sulfin* oxidation state offer virtually a new mechanism for each type of compound studied. This paper reports an extension of this generalization to optically active sulfinamides. The optical lability of sulfinamides in the solid state in the presence of sunlight was noted by others.[6] We have found that sulfinamides racemize in solution by a mechanism entirely different from those previously reported for sulfur in the *sulfin* oxidation state, and unique in the field of stereochemistry.

---

[1] This investigation was supported by the U. S. Public Health Service Research Grant No. GM12640-07 from the Department of Health, Education, and Welfare.

[2] The authors thank A. Nudelman [Ph.D. Thesis, UCLA, 1969] for preliminary observations.

[3] (a) K. Mislow, M. Axelrod, D. R. Rayner, H. Gotthardt, L. M. Coyne, and G. S. Hammond, *J. Amer. Chem. Soc.*, 87, 4958, 4959 (1965); (b) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *ibid.*, 88, 3138 (1966); (c) E. G. Miller, D. R. Rayner, and K. Mislow, *ibid.*, 88, 3139 (1966); (d) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *ibid.*, 86, 1452 (1964), and references cited therein.

[4] (a) D. Darwish and G. Tourigny, *ibid.*, 88, 4303 (1966); (b) D. Darwish and R. L. Tomilson, *ibid.*, 90, 5938 (1968).

[5] (a) P. Koch and A. Fava, *ibid.*, 90, 3867 (1968); (b) E. Cuiffarin, M. Isola, and A. Fava, *ibid.*, 90, 3594 (1968).

[6] S. Colonna, R. Giovini, and F. Montanari, *Chem. Commun.*, 865 (1968).