Table I. Effect of 2×10^{-2} *M* Diamino Acids, II, on the T_m of the Helix–Coil Transition of rI–rC, rA–rU, and Calf Thymus DNA in 0.025 *M* Sodium Phosphate Buffer (0.025 *M* in Na^+), pH 6.25, and 0.02 *M* NaCl

Compd	T_m, deg[a–c] rI–rC	rA–rU	Calf thymus DNA	No. of positive[d] charges/molecule at 25.0°	50.0°	75.0°
L-Diaminopropionic acid	63.0	51.3	78.3	1.76	1.57	1.37
L-Diaminobutyric acid	64.2	51.8	81.0	2.00	2.00	1.97
DL-Diaminobutyric acid	62.2	51.4	81.0	2.00	2.00	1.97
L-Ornithine	61.6	51.8	78.2	2.00	2.00	2.00
DL-Ornithine	59.4	51.8	78.0	2.00	2.00	2.00
L-Lysine	56.6	49.5	78.6	2.00	2.00	2.00
D-Lysine	56.1	49.4	77.9	2.00	2.00	2.00

[a] Melting curves were measured in 1-ml cuvettes thermostated with a Haake constant-temperature water circulator equipped with a Neslab temperature programmer. A Gilford Model 240 spectrophotometer equipped with automated recording accessories was used, and the temperature of the cell compartment was measured directly by using an iron-constantan thermocouple connected to a Leeds-Northrup Model 8290 potentiometer. [b] The T_m of the rI–rC (Miles Labs), rA–rU (Calbiochem), and calf thymus DNA (Calbiochem) in the absence of the diamino acids II are found to be 50.3 ± 0.4°, 44.6 ± 0.2°, and 73.4 ± 0.3°. (It should be noted that the previously reported T_m of rI–rC[3] and rA–rU[3] of 48.8 ± 0.4° and 46.4 ± 0.4°, respectively, refer to different lot number and source of material.) [c] T_m curves of the nucleic acid helices in the presence of the salts II were run concurrently for each pair, *i.e.*, L and DL mixtures. Under these conditions ΔT_m [T_m(L) − T_m(D or DL)] is found to be reproducible to within ±0.3°. [d] Titration curves of the diamino acids II in 0.025 *M* NaCl were performed using a Radiometer automatic titrator.

Table II. The Effect of 2×10^{-3} *M* Lysyl Dipeptides on the T_m of the Helix–Coil Transition of rI–rC, rA–rU, and Calf Thymus DNA in 0.025 *M* Sodium Phosphate Buffer (0.025 *M* in Na^+), pH 6.25[a–d]

Compd	T_m, deg[a–c] rI–rC	rA–rU	Calf thymus DNA	No. of positive[d] charges/molecule at 30.0°	50.0°
L-Lysyl-L-leucine	56.4	48.1	76.8	1.98	1.95
D-Lysyl-D-leucine	54.6	46.7	76.1	1.98	1.95
L-Lysyl-L-phenylalanine	53.2	46.3	75.2	1.91	1.84
D-Lysyl-D-phenylalanine	51.8	45.5	74.8	1.91	1.84
L-Lysylglycine	53.4	46.6	75.0	1.94	1.87

[a–d] Same as in Table I.

L-amino acids and the nucleic acid helical structure based on a chain composed of alternating D-pentose and phosphate residues?"[2] In an attempt to shed light on the second question, Gabbay and Kleinman[3] have shown recently that the L enantiomers of the amino acid amides of the general structure I, $^+NH_3CHRCONHCH_2CH_2NMe_2H^+2Br^-$, interact more strongly with nucleic acid helices than the corresponding D enantiomers. In this paper, we wish to report that the preference for the L enantiomers appears to be general for other amino acids and their derivatives. The effect of diamino acids of the general structure II, $^+NH_3CH(CO_2^-)(CH_2)_nN^+H_3 \cdot Cl^-$, and lysyl dipeptides III, $^+NH_3CH((CH_2)_4N^+H_3)CONHCHRCO_2^- \cdot Br^-$, on the melting temperature of polyriboinosinic–polyribocytidylic acids (rI–rC), polyriboadenylic–polyribouridylic acids (rA–rU), and calf thymus DNA is reported in Tables I[3] and II, respectively.

Several interesting points may be made. (1) There is very little difference in the degree of stabilization of polyriboadenylic–polyribouridylic (rA–rU) and calf thymus DNA helices by the L and DL mixture of the diamino acids II. However, there is a very large difference in the degree of stabilization of the polyriboinosinic–polyribocytidylic helix which is consistent with our earlier studies on this system.[3] (2) The degree of stabilization of the helices by the diamino acids II is considerably lower than the diammonium salts IV, $^+NH_3(CH_2)_nN^+H_3 \cdot 2Br^-$, due to the presence of the negatively charged carboxyl group.[4] (3) The effect of the neighboring negatively charged group is seen dramatically in the lysine system. For example, approximately the same degree of stabilization of the rI–rC and rA–rU helices are obtained by the lysyl dipeptides III at one-tenth the concentration of lysine (Tables I and II). (4) The LL-lysyl dipeptides stabilize the nucleic acid helices to a greater degree than the corresponding DD-lysyl dipeptides. Although the difference in the degree of stabilization of calf thymus DNA by the LL and DD enantiomers is not substantial, it is still outside the experimental error.

The nature of the difference between the interaction of the L and D enantiomers with nucleic acid helices is not clear. A general phenomenon is being observed, namely, a greater degree of stabilization of nucleic acid helices by the L-amino acid derivatives, *i.e.*, the amide salts I, $^+NH_3CHRCONHCH_2CH_2N^+Me_2H \cdot 2Br^-$, the diamino acids II, $^+NH_3CH(CO_2^-)(CH_2)_n \cdot N^+H_3 \cdot Cl^-$ where n = 2, 3, and 4, and lysyl dipeptides III, $^+NH_3CH((CH_2)_4N^+H_3)CONHCHRCO_2^- \cdot Br^-$. The results are clearly indicative of a selective interaction.[5]

Acknowledgment. This work was supported by the Rutgers Research Council and by Grants GM-13597 and GM-15308 from the U. S. Public Health Service. We wish to thank the National Science Foundation for a summer undergraduate fellowship to R. R. S.

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(2) H. Erying, L. L. Jones, and J. D. Spikes in "Horizon in Biochemistry," M. Kasha and B. Pullman, Ed., Academic Press Inc., New York, N. Y., 1962.

(3) E. J. Gabbay, *Biochemistry*, **5**, 3036 (1966); E. J. Gabbay, *Biopolymers*, **5**, 726 (1967); E. J. Gabbay and R. Kleinman, *J. Am. Chem. Soc.*, **89**, 7123 (1967).

(4) In the presence of 2×10^{-2} *M* IV in 0.025 *M* sodium phosphate buffer the T_m of the rI–rC is found to be 83.0, 83.6, and 78.0° for n = 2, 3, and 4, respectively.

(5) E. J. Gabbay, manuscript in preparation (1968).

(6) National Science Foundation Predoctoral Trainee, 1965–1968.

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Received February 5, 1698

The Radical-Catalyzed Rearrangement of Trisilanethiols[1]

Sir:

The transformation of hexamethyldisilane to trimethyl[(dimethylsilyl)methyl]silane, which occurs in the

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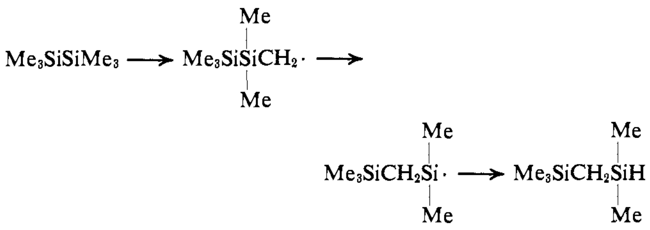
(1) This work was supported in part by the Electronic Technology Division of the Air Force Avionics Laboratory, Wright-Patterson Air Force Base, Ohio, under Contract No. AF-33(615)-67-C-1175.

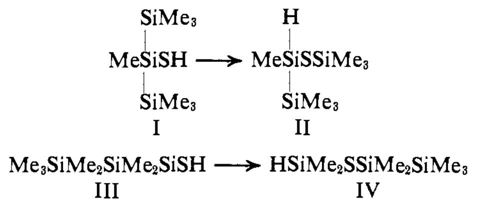
gas phase at 600°,[2] is considered to involve a 1,2 shift of the trimethylsilyl group of the intermediate (pentamethyldisilanyl)methyl radical[3] (Scheme I). By way of contrast, no skeletal rearrangement occurs when this radical is generated in solution, and only products of radical dimerization and halogen atom abstraction from the solvent are observed.[4] These results would imply that 1,2-trialkylsilyl shifts, in common with alkyl and hydrogen atom 1,2 shifts,[5] proceed *via* a transition state (or metastable intermediate) of relatively high energy. It is therefore of interest that we now find that trisilanethiols readily undergo a radical-induced skeletal rearrangement (Scheme II), providing the first examples of 1,2 shifts of the silyl and disilanyl groups which occur in solution under mild conditions.

Scheme I



$$\mathrm{Me_3SiSiMe_3} \longrightarrow \mathrm{Me_3Si}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}\mathrm{CH_2\cdot} \longrightarrow \mathrm{Me_3SiCH_2}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}\cdot \longrightarrow \mathrm{Me_3SiCH_2}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}\mathrm{H}$$

Scheme II



$$\mathrm{Me}\underset{\mathrm{SiMe_3}}{\overset{\mathrm{SiMe_3}}{\mathrm{Si}}}\mathrm{SH} \longrightarrow \mathrm{Me}\underset{\mathrm{SiMe_3}}{\overset{\mathrm{H}}{\mathrm{Si}}}\mathrm{SSiMe_3}$$

I II

$$\mathrm{Me_3SiMe_2SiMe_2SiSH} \longrightarrow \mathrm{HSiMe_2SSiMe_2SiMe_3}$$

III IV

Heptamethyltrisilane-2-thiol (I), bp 45° (0.45 mm), is conveniently prepared in 60–70% yields *via* the intermediate aminosilane by successive treatment of heptamethyltrisilanyl 2-chloride[6] in cyclohexane with gaseous ammonia and hydrogen sulfide. Its structure is verified by elemental analysis and infrared[7] ($\nu_{\max}^{\text{film}}$ 2960 s, 2900 m, 1440 sh, 1405 w, 1260 sh, 1250 s, 1100 w, 1025 w, 840 s, 785 s cm^{-1}) and nmr[8] (9.5 Hz, s, 18 H; 22.0 Hz, s, 3 H) spectral analysis. When a solution of the thiol (250 mg) in cyclohexane (2 ml) containing azobisisobutyronitrile (~1 mg) is heated to reflux, quantitative rearrangement[9] to an isomer occurs in less than 15 min. The rearrangement product was isolated by distillation (bp 43° (0.65 mm)) and unequivocably identified as 1-H-1-trimethylsilyltetramethyldisilthiane (II) on the basis of elemental analysis and infrared ($\nu_{\max}^{\text{film}}$ 2960 s, 2900 m, 2105 s, 1405 w, 1250 s, 890 sh, 840 s, 790 s cm^{-1}) and nmr (9 Hz, s, 9 H; 19.5 Hz, s, 21.5 Hz, J = 4.5 Hz, d, Σ12 H;[10] 272 Hz, q, 1 H, J = 4.5 Hz) spectral analysis. Furthermore, treatment with ethanol affords trimethylethoxysilane[11] and 1-H-1-ethoxytetramethyldisilane, the latter being isolated and characterized by elemental analysis and infrared (2075 cm^{-1}, SiH; 1110 and 1080 cm^{-1}, SiOC) and nmr (8 Hz, s, 9 H; 18.5 Hz, J = 4 Hz, d, 3 H; 71.5 Hz, J = 7 Hz, t, 3 H; 222 Hz, J = 7 Hz, q, 2 H; 289.5 Hz, J = 4 Hz, q, 1 H) spectral data.

Heptamethyltrisilane-1-thiol (III), bp 41° (0.65 mm), prepared from the corresponding chlorosilane,[12] undergoes rearrangement even more readily than the 2 isomer. It cannot be distilled without initiation of isomerization, although it may be stabilized in cyclohexane containing hydroquinone. Rearrangement may be reinitiated by addition of azobisisobutyronitrile and is completed in less than 5 min in refluxing cyclohexane. The structure of III (93% purity) follows from the method of preparation and infrared ($\nu_{\max}^{\text{film}}$ 2960 s, 2900 m, 1400 w, 1250 s, 835 s, 785 s), nmr (8.0 Hz, s, 9.5 Hz, s, Σ 15 H[10]; 22.5 Hz, s, 6 H) and ultraviolet absorption ($\lambda_{\max}^{\text{isooctane}}$ 219 mμ (ϵ 7200)) spectral data. The structure of the rearrangement product, 1-H-3-(trimethylsilyl)tetramethyldisilthiane (IV), is established by elemental analysis and infrared ($\nu_{\max}^{\text{film}}$ 2960 s, 2900 m, 2135 s, 1400 w, 1250 s, 880 s, 840 s, 790 s cm^{-1}), nmr (7.5 Hz, s, 9 H; 21.0 Hz, d, J = 3.5 Hz, 22.5 Hz, s, Σ 12 H;[10] 286.5 Hz, 1 H, heptet, J = 3.5 Hz), and ultraviolet absorption ($\lambda_{\max}$ <200 mμ) spectral data. Cleavage of IV with phosphorus trichloride affords dimethylchlorosilane[11] and pentamethylchlorodisilane.[11]

The initiation of the rearrangement by heat and by radical initiators such as benzoyl peroxide and azobisisobutyronitrile and its inhibition by a radical scavenger such as hydroquinone clearly indicate the involvement of a radical mechanism. Neither catalytic amounts of bases (methyllithium, potassium) nor Lewis acids (aluminum trichloride, boron trifluoride etherate) initiate the rearrangement. Considering the well-documented susceptibility of the sulfhydryl group to radical attack,[13] the initiation step in the rearrangement is considered to be hydrogen abstraction to form the (trisilanyl)thiyl radical (1). Following the 1,2 shift of the silyl group (2), hydrogen abstraction by the resulting silyl radical constitutes a propogation process (3).

$$\mathrm{Me_3SiMe_2SiMe_2SiSH} + \mathrm{R}\cdot \longrightarrow \mathrm{Me_3SiMe_2SiMe_2SiS}\cdot + \mathrm{RH} \quad (1)$$

$$\mathrm{Me_3SiMe_2SiMe_2SiS}\cdot \longrightarrow \cdot\mathrm{Me_2SiSSiMe_2SiMe_3} \quad (2)$$

$$\mathrm{Me_3SiMe_2SiMe_2SiSH} + \cdot\mathrm{Me_2SiSSiMe_2SiMe_3} \longrightarrow \mathrm{Me_3SiMe_2SiMe_2SiS}\cdot + \mathrm{HMe_2SiSSiMe_2SiMe_3} \quad (3)$$

Although a methyl group is also suitably situated for a 1,2 shift to the intermediate thiyl radical, no products attributable to such a shift could be detected by glpc or nmr analysis, or after the subsequent cleavage with phosphorus trichloride. Furthermore, triethylsilanethiol,[14] in which *only* an alkyl group can migrate, does

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(2) K. Shiina and M. Kumada, *J. Org. Chem.*, **23**, 139 (1958).

(3) H. Sakurai, R. Koh, A. Hosomi, and M. Kumada, *Bull. Chem. Soc. Japan*, **39**, 2050 (1966).

(4) H. Sakurai, T. Kishida, A. Hosomi, and M. Kumada, *J. Organometal. Chem.* (Amsterdam), **8**, 65 (1967).

(5) C. Walling in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 416. For examples of 1,2-hydrogen and -alkyl shifts involving diradicals, see D. I. Schuster and I. S. Krull, *J. Am. Chem. Soc.*, **88**, 3456 (1966), and C. McKnight and F. S. Rowland, *ibid.*, **88**, 3179 (1966), respectively.

(6) M. Kumada, M. Ishikawa, and S. Maeda, *J. Organometal. Chem.* (Amsterdam), **2**, 478 (1964).

(7) Determined using a Perkin-Elmer Model 221 infrared spectrometer with frequencies accurate to ±5 cm^{-1}.

(8) Determined as neat liquid using a Varian A-60 spectrometer and reported downfield from tetramethylsilane (internal standard).

(9) Determined by glpc, using a 183 cm × 6 mm column of 2% SE 52 on Chromsorb G.

(10) Integration of the separate signals was prevented because of partial overlap.

(11) Identified on the basis of glpc retention times.

(12) H. Sakurai, K. Tominaga, T. Watanabe, and M. Kumada, *Tetrahedron Letters*, 5493 (1966). This method of preparation affords ≈5% heptamethyltrisilanyl 2-chloride as a contaminant.

(13) For example, see G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," Collier-Macmillan Ltd., London, 1964, p 66.

(14) E. Larsson and R. Marin, *Acta Chem. Scand.*, **5**, 964 (1951).

not rearrange in refluxing cyclohexane or in refluxing xylene in the presence of azobisisobutyronitrile and benzoyl peroxide. These results are consistent with the proposed mechanism for, in contrast to cationic species, 1,2 alkyl shifts in radical species are not generally observed.[5]

The facility of 1,2 shifts has been usefully discussed within a molecular orbital framework.[5,15] The transition state (or metastable intermediate) is regarded to be a bridged or cyclic structure, which consequently has one bonding and two antibonding molecular orbitals. Using this model the cationic migration of an alkyl group is energetically permissible, the two electrons involved in the rearrangement being placed in the bonding orbital. However, the extra electron of the *radical* species must be placed in an antibonding orbital and the energy of the transition state then becomes prohibitive. This restriction need not apply in the case of silicon and other second-row elements[16] because of their ability to use energetically accessible d orbitals to accommodate the extra electron.[17]

Apart from its theoretical significance, the rearrangement of polysilanethiols provides the first synthetic method of stepwise degradation of a polydimethylsilane chain and, as demonstrated above, may also prove valuable in determining the position of substituents and the structure of isomeric polysilanes.

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(15) H. E. Zimmerman and A. Zweig, *J. Am. Chem. Soc.*, **83**, 1196 (1961); A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 380.

(16) For a recent summary, see P. S. Skell, "Organic Reaction Mechanisms," Special Publication No. 19, The Chemical Society, London, 1965, p 131; R. Kh. Freidlina, *Advan. Free Radical Chem.*, 1, 211 (1965).

(17) Examples of anionic 1,2 shifts of trialkylsilyl groups are already well documented in the rearrangement of silylhydrazines[18] and α-silylcarbinols.[19]

(18) R. West and M. Ishikawa, *J. Am. Chem. Soc.*, **89**, 4981 (1967), and references therein.

(19) A. G. Brook, *Pure Appl. Chem.*, 13, 215 (1966), and references therein.

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Received February 7, 1968

The Formation and Reactions of Monovalent Carbon Intermediates. II. Further Studies on the Decomposition of Diethyl Mercurybisdiazoacetate

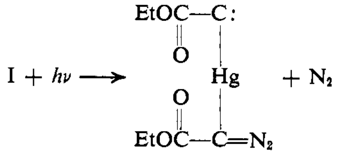
Sir:

We have recently reported the photolysis of diazomercurials[1] as a source of the novel carbyne radicals. Further studies on the photolysis and thermolysis of diethyl mercurybisdiazoacetate (I) have led to important findings that we wish to outline briefly.

A. Effect of Wavelength. Like diazoalkanes, I exhibits two absorptions above 2200 Å (λ_{max}^{EtOH} 3800 Å (ε 107) and 2640 Å (ε 24,900)).[1,2] Photolysis in these bands may conceivably lead to different primary steps. In the earlier study[1] irradiations were conducted in Vycor 7910 vessels with a medium-pressure mercury arc. Under these conditions excitation is predominantly (>90%) in the higher energy band, resulting most likely in

$$I + h\nu \longrightarrow 2N_2 + Hg + 2:\dot{C}CO_2Et \qquad (1)$$

We now find that photolysis with Pyrex-filtered light (λ >2800 Å) leads to an additional primary step

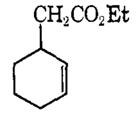


$$I + h\nu \longrightarrow \begin{array}{c} EtOC{-}C: \\ \| \quad | \\ O \quad \; \\ \quad Hg \\ O \quad | \\ \| \quad | \\ EtOC{-}C{=}N_2 \end{array} + N_2 \qquad (2)$$

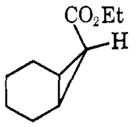
II

yielding the novel mercurycarbene[3,3a] II. Above 3350 Å, step 1 diminishes (Table I) and the reaction becomes a relatively clean source of II. It is tentatively suggested that the photolysis of I in the first (π,σ*) band proceeds *via* primary step 2 and in the second (π,π*) band *via* step 1.

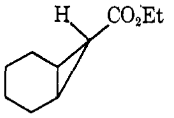
The carbyne formed in (1) reacts with cyclohexene[1] to give 3,3′-bicyclohexenyl (VI) and



III



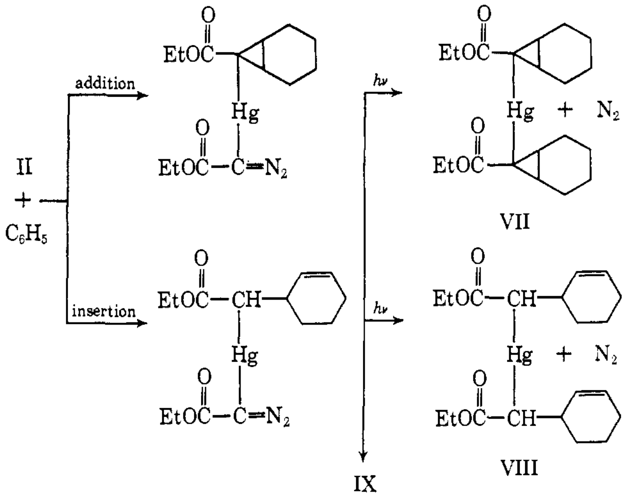
IV



V

and the mercurycarbene in (2) to give VII (stereostructure undetermined) along with C-H insertion (VIII) and mixed insertion-addition products (IX).

The following sequence appears to apply.



Insertion is probably into allylic C-H, with relative rates as compared to addition of 0.63 (λ >2800 Å) and 0.50 (λ >3350 Å).

Secondary photolysis of these mercurials with Pyrex-filtered light is insignificant as demonstrated by auxiliary experiments, and may not be the source of III-VI. However, photolysis of VII at shorter wavelengths in cyclohexene gave III-VI.

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(1) T. DoMinh, H. E. Gunning, and O. P. Strausz, *J. Am. Chem. Soc.*, **89**, 6785 (1967).

(2) The analogous absorptions of diazoalkanes correspond to σ* ← π and π* ← π transitions: R. Hoffmann, *Tetrahedron*, **22**, 539 (1966), and references therein.

(3) This is the first reported example of a metal carbene; the phosphorus analogs have been described recently. *Cf.* D. Seyforth, P. Hilbert, and R. S. Marmor, *J. Am. Chem. Soc.*, **89**, 4811 (1967).

(3a) NOTE ADDED IN PROOF. Schöllkopf and Rieber have postulated the photochemical formation of analogous Sn- and Si-containing structures in a recent communication: U. Schöllkopf and N. Rieber, *Angew. Chem.*, 79, 906 (1967).