yl-L-arginylglycyl-L-phenylalanyl-L-phenylalanyl-L-tyrosyl-L-threonyl-L-prolyl-N^{ϵ}-tosyl-L-lysyl-L-alanine methyl ester hydrochloride 0.5 hydrate (92 mg.) was dissolved in a mixture of acetic acid (6 ml.) water (2 ml.), and 1 N HCl (0.2 ml.) and hydrogenated for 6 hr. in the presence of 10% palladium–charcoal catalyst (0.1 g.). The catalyst was filtered off and the filtrate lyophilized. The resulting product was dried over P_2O_5 *in vacuo;* wt. 84 mg. (98%); $[\alpha]^{28}$D $-33.6°$ (c 0.19, 50% aqueous acetic acid); R_f^1 0.78, R_f^2 8.53 X his, single spot ninhydrin and Sakaguchi positive.

Anal. Calcd. for $C_{67}H_{94}N_{14}O_{17}SCl_2\cdot3H_2O$: C, 52.7; H, 6.60; N, 12.9. Found: C, 52.2; H, 6.88; N, 12.9.

Amino analysis of the decapeptide dihydrochloride by an automatic analyzer after acid hydrolysis showed the expected composition expressed in molar ratios: $lys_{0.94}arg_{0.90}thr_{1.04}glu_{1.12}pro_{1.08}gly_{1.04}ala_{1.04}tyr_{0.94}phe_{1.96}$. The average amino acid recovery was 93% of theory.

Amino acid analysis of an LAP digest showed the ratios[29]: $N^{\epsilon}\text{-tosyllys}_{0.57}arg_{1.00}thr_{1.04}pro_{0.96}gly_{1.00}ala_{1.00}tyr_{1.06}phe_{2.00}glu_{0.16}$; average recovery 89% of theory.

N^{α}-Carbobenzoxy-N^{ω}-tosyl-L-arginylglycyl-L-phenylalanyl-L-phenylalanyl-L-tyrosyl-L-threonyl-L-prolyl-N^{ϵ}-tosyl-L-lysyl-L-alanine Methyl Ester 1.5 Hydrate (VI).—N-Carbobenzoxyglycyl-L-phenylalanyl-L-phenylalanyl-L-tyrosyl-L-threonyl-L-prolyl-N^{ϵ}-tosyl-L-lysyl-L-alanine methyl ester hydrate (4.05 g.) was dissolved in methanol (60 ml.) containing 2 N HCl (2 ml.) and hydrogenated for 6 hr. over 10% palladium–charcoal catalyst (1.6 g.). The catalyst was filtered off and the filtrate concentrated to dryness *in vacuo.* The solid residue of octapeptide ester hydrochloride was dried by the addition of methanol followed by evaporation. The residue was then used directly for condensation with N^{α}-carbobenzoxy-N^{ω}-tosyl-L-arginine.

A solution of N^{α}-carbobenzoxy-N^{ω}-tosyl-L-arginine (1.48 g.) in acetonitrile (40 ml.) was cooled to 0° and triethylamine (0.46 ml.) was added followed by 2-ethyl-5-phenyloxazolium-3'-sulfonate (0.84 g.). After 1 hr. at 0° the reaction mixture was diluted with a solution of the octapeptide ester in dimethylformamide and acetonitrile prepared as noted: the hydrochloride salt, which had been made as described previously, was dissolved in a mixture of dimethylformamide (15 ml.) and acetonitrile (15 ml.) containing triethylamine (0.46 ml.), stirred 5 min., and then added to the reaction mixture prepared as described above. After 24 hr. at room temperature the reaction mixture was diluted with 0.5 N NaHCO$_3$ (250 ml.). The precipitated product was collected by filtration, washed successively with water, 1 N HCl, and water again. On reprecipitation from methanol–ether, 4.29 g. (87%) of product was obtained, m.p. undetermined; the peptide sinters at 125° and eventually it is converted to a liquid at 160°; $[\alpha]^{27}$D $-23.5°$ (c 0.17, dimethylformamide).

Anal. Calcd. for $C_{78}H_{95}N_{13}O_{18}S_2\cdot1.5H_2O$: C, 57.5; H, 6.28; N, 11.6. Found: C, 57.4; H, 6.40; N, 11.4.

The protected nonapeptide was decarbobenzoxylated on exposure to HBr in acetic acid and subjected to paper chromatography; R_f^1 0.92, R_f^2 6.8 X his, single ninhydrin positive spot. A sample of the decarbobenzoxylated nonapeptide was subjected to acid hydrolysis. Paper chromatography of the hydrolysate showed the presence of ninhydrin-positive spots with R_f^1's 0.14, 0.16, 0.22, 0.27, 0.33, 0.37, 0.46, and 0.63, identical with the R_f's of authentic samples of lysine, arginine, glycine, threonine, alanine, proline, tyrosine, and phenylalanine, respectively. The chromatogram exhibited also traces of two ninhydrin-positive spots with R_f^1 s 0.70 and 0.76 corresponding to the hydrochlorides of N^{ω}-tosylarginine and N^{ϵ}-tosyllysine, respectively.

Amino acid analysis of an acid hydrolysate of the decarbobenzoxylated nonapeptide by an automatic amino acid analyzer showed the ratios: $lys_{0.94}arg_{0.92}thr_{0.98}pro_{1.06}gly_{1.10}ala_{1.08}phe_{2.04}$; average amino acid recovery was 87% of theory.

N-Carbobenzoxy-γ-benzyl-L-glutamyl-N^{ω}-tosyl-L-arginylglycyl-L-phenylalanyl-L-phenylalanyl-L-tyrosyl-L-threonyl-L-prolyl-N^{ϵ}-tosyl-L-lysyl-L-alanine Methyl Ester (VII).—A suspension of N^{α}-carbobenzoxy-N^{ω}-tosyl-L-arginylglycyl-L-phenylalanyl-L-phenylalanyl-L-tyrosyl-L-threonyl-L-prolyl-N^{ϵ}-tosyl-L-lysyl-L-alanine methyl ester (4.5 g.) in acetic acid (18 ml.) was treated with 4 N HBr in acetic acid (18 ml.). After 1 hr. at room temperature, anhydrous ether (300 ml.) was added and the precipitated product was isolated by filtration, washed with ether, and dried over KOH *in vacuo.* To a solution of this product in dimethylformamide (30 ml.), triethylamine (1.2 ml.) was added followed by N-carbobenzoxy-γ-benzyl-L-glutamic acid p-nitrophenyl ester (1.42 g.). After 24 hr. the reaction mixture was diluted with 1 N KHCO$_3$ (3 ml.), stirred for 30 min., and poured into ice-cold 0.5 N NH$_4$OH (200 ml.). The precipitated product was filtered off, washed successively with 1 N NH$_4$OH, water, 1 N HCl, and water, and dried. On reprecipitation from methanol, 3.77 g. (70%) of product was obtained, m.p. 197–200°, $[\alpha]^{27}$D $-38.7°$ (c 0.20, dimethylformamide).

Anal. Calcd. for $C_{85}H_{108}N_{14}O_{21}S_2$: C, 60.0; H, 6.17; N, 11.1. Found: C, 59.7; H, 5.99; N, 10.7. For paper chromatography a sample was decarbobenzoxylated on exposure to HBr in acetic acid in the usual manner; R_f^1 0.91, R_f^2 8.93 X his, single ninhydrin positive spot.

Amino acid analysis of an acid hydrolysate of the decarbobenzoxylated peptide showed the expected composition expressed in molar ratios: $lys_{1.03}arg_{0.95}thr_{0.99}glu_{1.2}pro_{1.10}gly_{1.08}ala_{1.05}tyr_{0.50}phe_{2.10}$; average recovery 76% of theory.

The deblocked peptide was digested with LAP. The results of the digestion were discussed previously.

COMMUNICATIONS TO THE EDITOR

## The Free Radical-Catalyzed Disproportionation of Arylsilanes. A New Homolytic Aromatic Displacement Reaction

Sir:

Although the acid[1]- and base[2]-catalyzed and thermal[3] redistribution of substituents on a silicon are well known, no example involving radical intermediates has been reported. We wish to report that a rapid redistribution of phenyl and hydrogen on silicon occurs in a variety of phenylsilanes in the presence of conventional free radical sources.

$$\overset{*}{Ph}Si\!\equiv\; +\; HSi\!\equiv\; \xrightarrow{R}\; PhSi\!\equiv\; +\; H\overset{*}{Si}\!\equiv$$
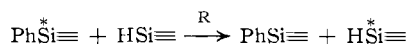
This reaction is a surprisingly efficient homolytic aromatic displacement reaction with silyl groups serving as both the attacking and leaving radicals.

(1) G. A. Russell, *J. Am. Chem. Soc.,* **81**, 4815 (1959).

(2) J. W. Ryan, *ibid.,* **84**, 4730 (1962).

(3) H. Gilman and D. H. Miles, *J. Org. Chem.,* **23**, 326 (1958).

Diphenylsilane undergoes extensive disproportionation on exposure to ultraviolet radiation at 70 to 130° or on warming to 130° with a variety of peroxy or azo initiators.

$$Ph_2SiH_2 \rightleftharpoons Ph_4Si + Ph_3SiH + PhSiH_3 + SiH_4$$
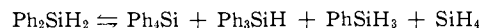
No reaction occurs at these temperatures in the absence of the initiator. The data in Table I give the extent of this reaction with some representative initiators. The dialkylperoxides appear to be the most efficient catalysts[4] with minimum kinetic chain lengths of over 60.[5]

As seen from Table II, a variety of phenylalkylsilanes undergo this radical-catalyzed reaction. No evidence for the redistribution of alkyl groups was observed.

(4) As the data in Table II show increasing chain length with higher temperature, the higher decomposition temperature of the dialkylperoxides is an advantage. These peroxides are also normally less susceptible to induced decomposition which could be a serious side reaction of the electrophilic silyl radical.

(5) The moles of Ph$_2$SiH$_2$ consumed per possible initiating radical from Table I. This calculation ignores the reverse reaction (Ph$_3$SiH + PhSiH$_3$ → 2Ph$_2$SiH$_2$) and is thus a minimum figure.

TABLE I

DISPROPORTIONATION OF DIPHENYLSILANE WITH VARIOUS INITIATORS

Initiator[a] and wt. %	Time, hr.	Temp., °C.	Rearrangement products, mole % in parentheses[b]
Ultraviolet light	72	70–130	Ph_3SiH (29), $PhSiH_3$ (13), SiH_4 (fire)[c]
dTBP (1)[d]	1.3	130	Ph_3SiH (40), $PhSiH_3$ (17), SiH_4 (3)
dTBP (0.25)	1.5	130	Ph_3SiH (20), $PhSiH_3$ (17), SiH_4 (1.5)
L101 (1)	1.3	130	Ph_3SiH (39), $PhSiH_3$ (18), SiH_4 (3)
AIBN (1)	1.3	130	Ph_3SiH (14), $PhSiH_3$ (8)
TBPB (1)	1.3	130	Ph_3SiH (11), $PhSiH_3$ (7)
Bz_2O_2 (1)	2.6	130	Ph_3SiH (7), $PhSiH_3$ (3)
None	1.3	130	None

[a] dTBP = di-t-butyl peroxide, L101 = 2,5-dimethyl-2,5-di-t-butylperoxyhexane, AIBN = 2,2'-azo-bis(2-methylpropionitrile), TBPB = t-butyl perbenzoate, Bz_2O_2 = benzoyl peroxide.   [b] Reagent and catalyst were heated in sealed n.m.r. sample tubes and the ratio of products determined by integration of the Si–H n.m.r. signals from the contents of the tube.   The yields of silane are low due to concentration of this product in the vapor above the liquid in the tubes.   The n.m.r. spectra showed no Si–H compounds other than those listed in the table nor were any other products except a small amount of tetraphenylsilane observed by v.p.c. analyses.   [c] This experiment was conducted in a Vycor tube and the contents were transferred to an n.m.r. sample tube for analyses.   The silane was lost (ignited on contact with air) on opening the Vycor tube.   [d] The molar ratio of $PhSiH_3$ to Ph_3SiH was unity during the early stages of this reaction, but dropped well below one due to further redistribution of $PhSiH_3$ as the reaction proceeded beyond ~20% conversion of Ph_2SiH_2.

TABLE II

FREE RADICAL-CATALYZED DISPROPORTIONATION OF SILANES

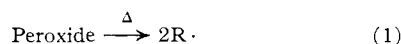| Silane	Time, hr.	Temp., °C.	Catalyst and %	Redistribution products,[a] mole % in parentheses
Ph_2SiD_2	1.3	130	dTBP (1)	$PhSiD$ (16), $PhSiD_3$ (17)[b]
$PhMeSiH_2$	1.0	160	dTBP (1)	Ph_3SiMe (trace), Ph_2MeSiH (35), $MeSiH_3$ (21)[c]
Ph_2MeSiH	1.0	160	dTBP (1)	Ph_3SiMe (25), $PhMeSiH_2$ (18)
$PhMe_2SiH$	1.6	160	dTBP (1)	Ph_2SiMe_2 (19), Me_2SiH_2 (9)[c]
m-$CH_3C_6H_4SiMe_2H$	3.0	180	L101 (3)	(m-$CH_3C_6H_4)_2SiMe_2$[d] (16), Me_2SiH_2 (8)[c]
$C_6H_5CH_2SiMe_2H$	1.0	160	dTBP (1)	None
o-$CH_3C_6H_4SiMe_2Pr$ + $EtMe_2SiH$	1.0	160	dTBP (1)	None

[a] The experimental procedure described in Table I with analyses by n.m.r. and v.p.c.   [b] No n.m.r. signal for any SiH compounds was observed.   [c] The yields of $MeSiH_3$ and Me_2SiH_2 are low due to the concentration of these products in the vapor above the liquid contents of the n.m.r. sample tube.   [d] The di-m-tolyldimethylsilane was separable by v.p.c. from all other isomeric ditolyldimethylsilanes.

Increasing alkyl substitution on the silicon markedly decreases the chain efficiency of this reaction at a given temperature. For example, diphenylsilane disproportionated rapidly at 130° with di-$tert$-butyl peroxide (dTPB), but the efficient disproportionation of phenyldimethylsilane with dTBP required 160°. No exchange was observed between trialkylsilanes and trialkylphenylsilanes with dTBP at 160°. No rearrangement or disproportionation of benzyldimethylsilane occurred under these conditions.[6]

The need for a radical source and the efficiency of the peroxides suggests a free radical chain process. The known susceptibility of the hydrogen on silicon toward abstraction by an alkyl or alkoxyl radical[8] and the absence of benzene as a product suggests that a silyl rather than an aryl radical is the chain carrying species. Additional insight into the step involving the cleavage of the phenyl–silicon bond is provided by the absence of position isomerization during the redistribution of tolyl groups and the absence of C–H, Si–D exchange during the disproportionation of diphenylsilane-d_2. Thus, the position of attachment of the silicon to the aromatic ring is unaltered during reaction and disilylcyclohexadienes formed via addition of a silane to the aromatic nucleus are clearly eliminated as intermediates.

These data suggest a mechanism involving direct displacement of a silyl group from the aromatic nucleus by a silyl radical as shown below
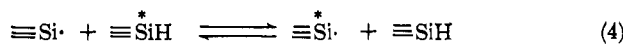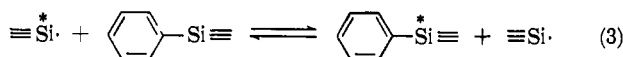
Initiation

$$\text{Peroxide} \xrightarrow{\Delta} 2R\cdot \qquad (1)$$

$$R\cdot + \equiv \overset{*}{Si}H \longrightarrow RH + \equiv Si\cdot \qquad (2)$$

Propagation

$$\equiv Si\cdot + \equiv \overset{*}{Si}H \rightleftharpoons \equiv \overset{*}{Si}\cdot + \equiv SiH \qquad (4)$$

This scheme is analogous to that proposed by Miller and Walling[9,10] for the reaction of aryl halides with halogen atoms.

All previous examples of homolytic aromatic displacements where the displaced group leaves as a chain carrying radical have involved chlorine, bromine, iodine, or sulfur radicals as the attacking and leaving radical.[9,10] No analogous intermolecular displacements with a carbon or oxygen radical as the attacking or leaving species is known.[11] This dramatic difference between the behavior of silyl radicals and their carbon analogs adds to the mounting evidence that this type of radical displacement reaction is very common with, and perhaps limited to, second or higher row elements.

The role of π complexes of the silyl radical and the aromatic ring in this reaction and the extension of this reaction to related elements are under investigation.

(9) B. Miller and C. Walling, J. Am. Chem. Soc., 79, 4187 (1957).

(10) B. Milligan and R. L. Bradow, J. Phys. Chem., 66, 2118 (1962), and references therein.

(11) The arylation or alkylation of a substituted benzene by an alkyl or aryl radical proceeds via displacement of a hydrogen rather than any other substituent such as halogen or carbon from the aromatic ring.[12] Also, this displacement of hydrogen occurs not by the ejection of a hydrogen atom but by disproportionation and other reactions of stable intermediate cyclohexadienyl radicals.[13]

(12) D. R. Augood and G. H. Williams, Chem. Rev., 57, 123 (1957).

(13) E. L. Eliel, S. Meyerson, Z. Welvart, and S. H. Wilson, J. Am. Chem. Soc., 82, 2936 (1960).

(6) Although β-phenylethyl radicals often rearrange via a 1,2-phenyl shift,[7] no phenyltrimethylsilane was formed from benzyldimethylsilane.

(7) W. H. Urry and M. S. Kharasch, J. Am. Chem. Soc., 66, 1438 (1944).

(8) C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960, p. 116.

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