on determination of yields of a number of products from methanol and their dependence on reaction conditions postulates that the intercepted species is the product of an insertion reaction.[6]

That N(^{4}S) does not attack water significantly is indicated by rates of formation of NH_2OH and "total nitroxyl" ($NO_2 + N_2O + NH_2OH$) which are not more than 0.01 and 0.1%, respectively, of the flow rate of N(^{4}S). That TNM is not attacked by active nitrogen itself is suggested by the fact that its rate of reduction to nitroform[7] when present in saturated aqueous solution (~5 m*M*) in the absence of alcohols is only 2% of the flow rate of N(^{4}S). The same ratio of rate of formation of Fe(III) to flow rate of N(^{4}S) is observed in the reaction of Fe(II) in 0.8 *N* H_2SO_4.[8] Both these reactions appear to involve attack by H atoms[7,9] produced in the decomposition of water vapor by $N_2(A\,^3\Sigma_u^+)$[3]. The inference that N(^{4}S) does not react with TNM is supported by the observation that the variation of the rate of production of HCN from methanol with change in concentration of methanol is paralleled by the variation in the rate of production of ethylene glycol, the principal product which replaces it in the presence of TNM. The precursor of HCN which is scavenged by TNM cannot be a free CH_2OH radical since this would be oxidized rapidly[7a] to formaldehyde. In the absence of TNM, ethylene glycol is a minor product. The increase in its limiting rate of production in the presence of TNM, corrected for direct oxidation of methanol to ethylene glycol by TNM, is equal within experimental error to the limiting rate of formation of HCN in the absence of TNM.

Active nitrogen was generated in a fast flow system[10] by irradiation with 2450-MHz microwaves. Its flow rate as determined by NO titration[11] at a point 1 cm above the water was 50×10^{-2} μmol sec^{-1}. The reaction flask was immersed in a bath maintained at 9 ± 1°. Yields of nitroform were determined by taking ϵ of its anion at 350 nm to be 1.48×10^4 M^{-1} cm^{-1}.[7b] Formaldehyde,[12] ethylene glycol,[13] and HCN[14] were determined by standard methods. Reaction times were 5 min. Yields of various products, expressed below in units of 10^{-2} μmol sec^{-1}, were constant at concentrations of methanol from 1 to 10 *M* and diminished gradually at lower concentrations, whether or not TNM was present. In the plateau region, yields from CH_3OH in the absence of TNM were: HCN, 20; CH_2O, 8; $(CH_2OH)_2$, 2. Under identical conditions, except that saturation with TNM was maintained, the yields were: HCN, <0.2; CH_2O, 11; $(CH_2OH)_2$, 30; $HC(NO_2)_3$, 8.5. Under the latter conditions, except that the discharge was not used, so that active nitrogen was absent, yields due to oxidation of CH_3OH by TNM were: CH_2O, <0.5; $(CH_2OH)_2$, 6; $HC(NO_2)_3$, 0.6. Yields of HCN from 2 *M* solutions of C_2H_5OH, $(CH_3)_2CHOH$, and $(CH_3)_3COH$ were, respectively, 20, 14, and 7. No HCN was detectable from such solutions when saturated with TNM and yields of nitroform were 22 from isopropyl alcohol and 18 from *tert*-butyl alcohol. That 2 *M* concentrations correspond to plateau conditions was established for the latter two alcohols.[15]

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(6) This analysis will be presented in the full report of this work.

(7) For the background of this experiment see (a) K. D. Asmus, A. Henglein, M. Ebert, and J. P. Keene, *Ber. Bunsenges. Phys. Chem.*, **68**, 657 (1964); (b) B. H. J. Bielski and A. O. Allen, *J. Phys. Chem.*, **71**, 4544 (1967); (c) J. Rabani, W. A. Mulac, and M. S. Matheson, *ibid.*, **69**, 53 (1965).

(8) Unpublished work by J. A. Goldberg in this laboratory.

(9) In the case of reaction with Fe(II) the yield of Fe(III) responds to variation of acid concentration in the same way as has been reported for oxidation of Fe(II) by H atoms; see G. Czapski and G. Stein, *J. Phys. Chem.*, **63**, 850 (1959).

(10) See A. Fujino, S. Lundsted, and N. N. Lichtin, *J. Amer. Chem. Soc.*, **88**, 775 (1966), for a description of apparatus and procedures. In the present work the gas stream was introduced about 1 cm below the surface of the well-stirred solution.

(11) P. Harteck, G. Mannella, and R. R. Reeves, *J. Chem. Phys.*, **29**, 608 (1958).

(12) C. E. Bricker and H. R. Johnson, *Ind. Eng. Chem., Anal. Ed.*, **17**, 400 (1945).

(13) N. N. Lichtin, *J. Phys. Chem.*, **63**, 1449 (1959).

(14) J. M. Kruse and M. J. Mellon, *Anal. Chem.*, **25**, 446 (1953).

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Novel Intramolecular Aryl Migrations from Carbon to Silicon by a Free-Radical Mechanism. Migration *vs.* Cyclization[1]

Sir:

Although migration of the phenyl group is the major reaction pathway in carbon-centered radicals, no example of rearrangement of radicals involving silicon or the other group IVb elements has been reported. Nelson, Angelotti, and Weyenberg[2] found that the phenyl groups in benzyldimethylsilyl radicals did not undergo 1,2 shifts. Wilt, Kolewa, and Kraemer[3] have recently disclosed that no migration of phenyl groups takes place in the intermediate triphenylsilylmethyl radical produced from triphenylsilylacetaldehyde at 150°. Thus, phenyl groups do not seem to undergo 1,2 shifts either to or from silicon. Also, in the case of silyl radicals derived from hydrosilanes of general formula $ArCH_2YCH_2SiMe_2H$ (Y = CH_2 or $SiMe_2$), no migration of the phenyl group took place, only the cyclization product being obtained.[4]

In this communication, the first example of phenyl migration to a silicon-centered radical is reported.[5] A mixture of (4-phenylbutyl)dimethylsilane [**1a**, bp 117° (20 mm); $n^{20}\mathrm{D}$ 1.4929; $d^{20}{}_4$ 0.8727] and di-*tert*-butyl peroxide (DTBP) in a molar ratio of 1:0.343 was placed in a sealed tube with degassing, and allowed to react in a constant-temperature bath kept at 135.0° for 15 hr. From a combination of nmr and ir spectra and vpc retention times the rearrangement product, *n*-butyldimethylphenylsilane [**2a**, bp 106° (19 mm); $n^{20}\mathrm{D}$ 1.4925; $d^{20}{}_4$ 0.8733], and the cyclization product, 1,1-dimethyl-2,3-benzo-1-silacyclohept-2-ene [**3a**, nmr (CCl_4) τ 9.65 (s, 4 H), 9.10–9.35 (m, 2 H), 8.10–8.50 (m, 4 H), 7.00–7.35 (m, 2 H), 2.45–2.90 (m, 4 H)],

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(1) Silyl Radicals. VII. For part VI, see H. Sakurai and M. Yamagata, *Chem. Commun.*, 1144 (1970).

(2) L. E. Nelson, N. G. Angelotti, and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **85**, 2662 (1963).

(3) J. W. Wilt, O. Kolewa, and J. F. Kraemer, *ibid.*, **91**, 2624 (1969).

(4) H. Sakurai, A. Hosomi, and M. Kumada, *Tetrahedron Lett.*, 1757 (1969).

(5) Thermal phenyl migrations in certain ω-phenylalkylsilanes in vapor phase have been reported recently although the mechanistic details remain uncertain: H. Sakurai, A. Hosomi, and M. Kumada, *Chem. Commun.*, 521 (1969).

were identified and found in the ratio 30.9:69.1. The structure of **3a** was further confirmed by transformation to (4-phenylbutyl)dimethylchlorosilane [bp 148° (19 mm), $n^{20}\text{D}$ 1.4999, $d^{20}{}_4$ 0.9951]. To our knowledge this is the first clear evidence that shows free-radical migration of the phenyl group from carbon to silicon. The ratio of the products depends on the molar ratio of the starting hydrosilane to DTBP and the results are shown in Table I. Similar results with (4-*p*-tolylbutyl)dimethylsilane [**1b**, bp 132° (17 mm), $n^{20}\text{D}$ 1.4917, $d^{20}{}_4$ 0.8684] and (4-phenylpentyl)dimethylsilane [**1c**, bp 108° (5 mm), $n^{20}\text{D}$ 1.4940, $d^{20}{}_4$ 0.9779] are also listed in Table I.

Table I. Reaction of (4-Arylbutyl)dimethylsilanes with DTBP at 135.0°

Substrate	DTBP/ substrate (molar ratio)	Rearrangement product, %	Cyclization product, %
$C_6H_5(CH_2)_4SiMe_2H$ (**1a**)	0.343	30.9	69.1
	0.767	25.5	74.5
	1.372	21.2	78.8
p-$CH_3C_6H_4(CH_2)_4SiMe_2H$ (**1b**)	0.423	37.8	62.2
	0.708	33.6	66.4
	1.113	28.0	72.0
	2.012	23.7	76.3
$C_6H_5CH(CH_3)(CH_2)_3SiMe_2H$ (**1c**)	0.697	72.0	28.0
	0.760	69.2	30.8

We have examined further a number of other compounds of a general formula of $PhCHY(CH_2)_nSiMe_2H$ for a possible competition of rearrangement *vs.* cyclization. Table II lists the results. For compounds of $n = 0, 1, 4$, and 5, neither cyclization nor rearrangement was observed. Only cyclization occurred for compounds of $n = 2$ as reported previously.[4] It is interesting to note that homolytic aromatic substitution, affording a five-membered ring compound which is not sterically much strained, is completely suppressed.

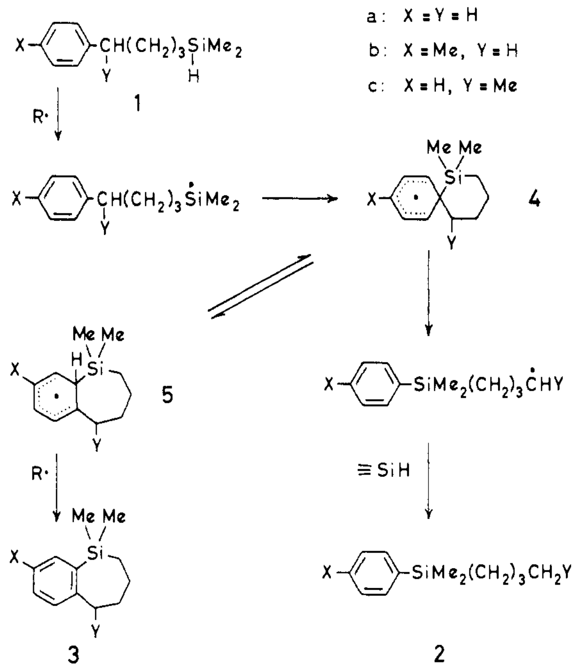
Table II. Reaction of $C_6H_5CHY(CH_2)_nSiMe_2H$ with DTBP at 135.0°

Substrate	n	Y	Rearrangement	Cyclization
7a	0	H	No	No
7b	0	Me	No	No
7c	0	Ph	No	No
8	1	H	No	No
6a	2	H	No	Yes
6b	2	Me	No	Yes
6c	2	Ph	No	Yes
1a	3	H	Yes	Yes
1c	3	Me	Yes	Yes
9	4	H	No	No
10	5	H	No	No

These results now suggest the following mechanism (Chart I) for the competition of rearrangement *vs.* cyclization of **1** involving a spirocyclohexadienyl radical (**4**) as an intermediate.

For compounds **1**, there may exist a subtle equilibrium between **4** and **5**. It is notable in this connection that increasing the amount of DTBP in reaction mixtures resulted in an increased amount of cyclization products and that introduction of a methyl group into the benzylic position favored the rearrangement. However, for compounds of $n = 2$ (**6**), the corresponding intermediate spiro radicals may collapse rapidly to cyclic intermediates corresponding to **5** leading to cyclization, since the ring size favors the latter radicals. The fact that neither rearrangement nor cyclization took place at all with $ArCHY(CH_2)_nSiMe_2H$, where $n = 0, 1, 4$, and 5, is also compatible with the intermediacy of the spiro radicals, since the formation of spiro intermediates of three-, four-, seven-, and eight-membered rings must be sterically strained.

Chart I



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Photochemically Induced Rearrangement of Ketene *via* an Oxirene Intermediate

Sir:

The photolysis of ketene has been studied for many years, sometimes because of its own inherent interest and more often in a peripheral manner to its use as a source of methylene radicals.[1] Detailed experiments have shown the presence of long-lived excited states through quantum yields for photodecomposition less than unity and variable with wavelength, pressure, and temperature for absorbed wavelengths ≥ 3130 Å.[2]

(1) (a) W. B. Demore and S. W. Benson, *Advan. Photochem.*, 2, 219 (1964); (b) J. A. Bell, *Progr. Phys. Org. Chem.*, 2, 1 (1964); (c) H. M. Frey, *Progr. Reaction Kinet.*, 2, 131 (1964); (d) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

(2) A. N. Strachan and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, 76, 3258 (1954); G. A. Taylor and G. B. Porter, *J. Chem. Phys.*, 36, 1353