Table I. Incorporation of Precursors into Ergosta-4,6,8(14),22-tetraen-3-one in *Penicillium rubrum*

Precursor	Spec act., counts sec^{-1} $mmol^{-1}$	Spec act. of **2**,[a] counts sec^{-1} $mmol^{-1}$	Incorporation, %
7	2.52×10^5	8.29×10^3	3.3
10	2.75×10^5	1.70×10^3	0.7
11	6.37×10^4	3.27×10^2	0.5
12	2.53×10^4	1.70×10^3	6.7

[a] These data include a correction for quenching of the fluorescer (PPO) by **2**.

shortwave uv light. Cultures were generally harvested after 13–18 days, and pure **2** was isolated by extraction with $CHCl_3$, followed by chromatography on alumina, eluting with heptane–ether (3:1). Quantitative assay of **2** was obtained from its absorption band at 348 nm (ϵ 26,500). Results of feeding experiments are presented in Table I. It was verified that precursors were incorporated into **2** without significant metabolic degradation by isolation of **2** from a feeding experiment with [^3H]ergosterol and reduction with Li–NH_3 to ergosterone (**4**). Base-catalyzed exchange of **4** removed >97% of label, affirming that tritium had been confined to C-4 and C-6 throughout biosynthesis.

Incorporation data support ergosterol as a precursor of **2** and provide evidence for a pathway involving oxygenation and dehydration. The relatively efficient incorporation of triol **12** could be accommodated by a sequence in which oxidation to the 3-keto-5α,8α-diol is followed by double elimination and, in this connection, it is noteworthy that a formal cis removal of water takes place at C-8,14.[17] As an *in vitro* model for this process, it was found that treatment of **13** with CrO_3–pyridine afforded **2** (and **8**) directly, by a route which probably involves allylic rearrangement of the intermediate chromate ester. Ergosterol peroxide (**10**) is also incorporated into **2**, though less efficiently than either **12** or ergosterol itself. In duplicate runs, the ratio of incorporation **10**:**7** remained constant at 0.2. Equivalent incorporation of **10** and **11** implies that **10** is not a *direct* precursor of **12**, and it is expected that experiments in progress will define more precisely the roles of these peroxides in the biosynthetic scheme. The acceptance by *P. rubrum* of 3-keto and 3β-ol functionality in this system is in accord with the demonstrated capacity of certain organisms for assimilation of unnatural substrates of the sterol type.[18] A search of the growth medium for likely biosynthetic intermediates, which has been carried on concurrently, has indicated the presence of **9** in *P. rubrum* cultures, and we also believe it significant that ergosterol and its peroxide have been found along with **2** in cultures of *Lampteromyces japonicus*.[5b]

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[17] A recent study of ergosterol biosynthesis has revealed that a 5α-hydroxy-Δ^7-sterol precursor [R. W. Topham and J. L. Gaylor, *Biochem. Biophys. Res. Commun.*, 27, 644 (1967)] yields **3** by cis elimination of the 6α hydrogen (personal communication from Professor J. L. Gaylor).

[18] D. H. R. Barton, D. M. Harrison, G. P. Moss, and D. A. Widdowson, *J. Chem. Soc. C*, 775 (1970).

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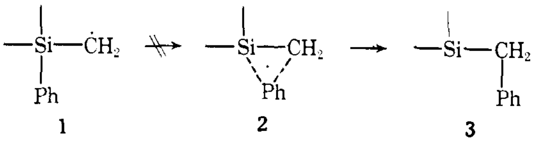
The Search for Radical Rearrangement in Organosilicon Systems. II. Silicon to Carbon Ar_1-5 and Ar_1-6 Phenyl Shifts

Sir:

In contrast to their all-carbon congeners, silaneophyl radicals **1** fail to rearrange.[1,2] It was suggested[1] that this lack of rearrangement of α-silyl radicals may be a consequence of their stabilization *via* d_π–p_π "back-bonding"[3] and the destabilization of the requisite state for such rearrangement (**2**) because of the strain predicted[1] for the (unknown) silacyclopropane ring.


1 **2** **3**

We were therefore prompted to remove both the anti-rearrangement factors associated with **1** and to study *farther* rearrangements in homologs of the silaneophyl type. We report here the first rearrangements of this type in organosilicon systems.[4]

Sequential treatment of 3-chloropropyltrichlorosilane with 1 equiv of phenyl Grignard reagent and 2 equiv of methyl Grignard reagent produced γ-(phenyldimethylsilyl)propyl chloride (**4**; 45.5%; bp 87–89° (1 mm); λ_{neat} 7.0, 9.0 (Ph–Si), 8.0 (CH_3–Si–CH_3); $\delta_{CCl_4}^{TMS}$ 3.28 t (–CH_2Cl)).[5,6] Addition of phenyldimethylsilane to 4-chloro-1-butene in the presence of chloroplatinic acid[7]

$$Cl_3SiCH_2CH_2CH_2Cl \xrightarrow[2.\ CH_3MgI]{1.\ PhMgBr} \underset{\mathbf{4}}{PhSi(CH_3)_2CH_2CH_2CH_2Cl}$$

yielded δ-(phenyldimethylsilyl)butyl chloride (**5**; 50%; bp 79–80° (0.1 mm); λ_{neat} 7.0, 9.0 (Ph–Si), 8.0 (CH_3–Si–CH_3); $\delta_{CCl_4}^{TMS}$ 3.37 t (–CH_2Cl)).[6]

$$Ph(CH_3)_2SiH + CH_2{=}CHCH_2CH_2Cl \xrightarrow{H_2PtCl_6} \underset{\mathbf{5}}{PhSi(CH_3)_2CH_2CH_2CH_2CH_2Cl}$$

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[1] Paper I: J. W. Wilt, O. Kolewe, and J. F. Kraemer, *J. Amer. Chem. Soc.*, 91, 2624 (1969). For the preliminary account, see J. W. Wilt and O. Kolewe, *ibid.*, 87, 2071 (1965).

[2] K. Yamamoto, K. Nakamishi, and M. Kumada, *J. Organometal. Chem.*, 7, 197 (1967).

[3] Because α-silyl radicals (and other group IV analogs) are formed in an esr study under conditions where all-carbon radicals are not, P. J. Krusic and J. K. Kochi (*J. Amer. Chem. Soc.*, 91, 6161 (1969)) deduce a special stability for the former attributable to d_π–p_π delocalization.

[4] For other types of radical rearrangement in silicon-containing species, see ref 1.

[5] This chloride is a minor product observed in the catalyzed addition of phenyldimethylsilane to allyl chloride: Z. V. Belyakova, M. G. Pomerantseva, and S. A. Golubstov, *Zh. Obshch. Khim.*, **36**, 1048 (1965).

[6] The compound gave an acceptable combustion analysis and its ir and nmr spectra were in accord with the structure given.

[7] N. M. Tomiuk, M.Sc. Thseis, Loyola University of Chicago, 1968.

The reduction of chlorides **4** and **5** with tri-*n*-butyltin hydride in the presence of di-*tert*-butyl peroxide produced the *n*-alkylsilanes, *but rearranged silanes were also observed.* Thus, from **4**, phenyldimethyl-*n*-propylsilane (**6**)[1] and the rearranged (γ-phenylpropyl)dimethylsilane (**7**; λ_{neat} 4.74 (Si–H), 8.0 (CH_3–Si–CH_3); $\delta^{\text{TMS}}_{\text{CCl}_4}$ 3.88 nonet (Si–H), 2.59 t (Ph–CH_2))[8] were formed. Similarly, from **5**, phenyldimethyl-*n*-butylsilane (**8**)[6,9] and the rearranged (δ-phenylbutyl)dimethylsilane (**9**;[6] λ_{neat} 4.75 (Si–H), 8.0 (CH_3–Si–CH_3); $\delta^{\text{TMS}}_{\text{CCl}_4}$ 3.90 nonet (Si–H), 2.58 t (Ph–CH_2)) were produced. Silaneophyl chloride under the same conditions gave no rearrangement.[10]

Control studies of these reactions indicated that the products were stable under the reaction conditions and that no reaction occurred in the absence of the tin hydride at the concentrations employed.

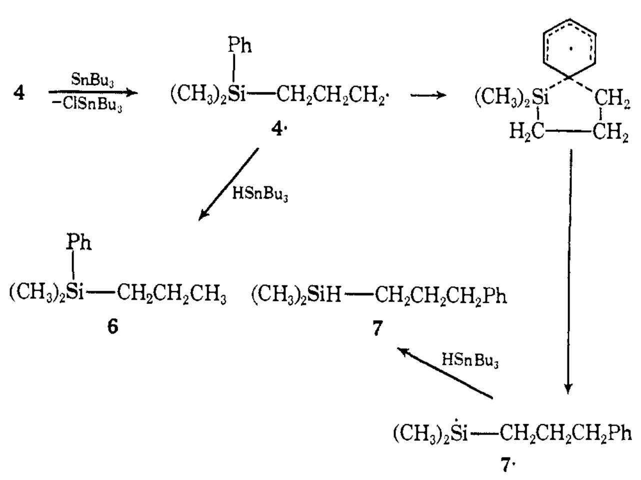
An increase in rearrangement was observed with dilution of the chlorides **4** and **5**, as shown in Table I.

Table I

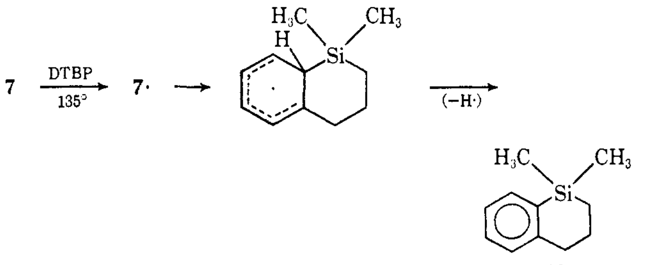
Chloride	M[a]	Rearranged product[b]	%[c]
4	1.0	**7**	0
4	0.1	**7**	2.5
4	0.01	**7**	23.5
5	1.0	**9**	0
5	0.1	**9**	4.5
5	0.01	**9**	13.0

[a] The reactions were performed in purified benzene in the presence of di-*tert*-butyl peroxide (DTBP) at 130–135°. The solutions were placed in ampoules and sealed *in vacuo* after three freeze–thaw cycles. The ratio of reactants was **4**(**5**):tri-*n*-butyltin hydride:DTBP = 30:10:3. The reactions were conducted for 15 hr and all the tin hydride was consumed. [b] The reactions were apparently quite clean. The only other products were the unrearranged silanes **6** and **8**, along with tri-*n*-butyltin chloride. [c] Percentage composition as determined by glpc on a polypropylene glycol adipate column at 150°. Duplicate runs indicated a precision of ±3%.

The present data suggest that, unlike their α-silyl counterparts,[1,2] γ- and δ-silyl radicals rearrange with no difficulty. Clearly, neither d_π–p_π back-bonding nor serious steric hindrance to transition state formation is now present, so the disparity between the organic and organosilyl systems, previously so apparent in the α radicals, disappears.[11] A plausible mechanistic scheme involving an Ar_1-5 phenyl shift is illustrated below for chloride **4**. An analogous one involving an Ar_1-6 phenyl shift would apply to **5**.



It should be noted that the reverse rearrangement of radical **7**· to radical **4**· does not occur. Rather, the decomposition of equimolar **7** and di-*tert*-butyl peroxide without solvent takes an Ar_2-6 course and leads to the silatetralin **10** at 135°.[12] No **10** was detected in our study of chloride **4**, nor was a similar ring-closed product found from chloride **5**.[13] In another study, Kumada and coworkers[14] reported the isomerization of **7** to **6** at 370°. If this thermal process involves radical **7**·, then the above change **4**· → **7**· must be reversed under these conditions.



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While further study must be done to sort out these differing processes, the present results indicate that organosilyl analogs of carbon neophyl radical rearrangements are not *per se* interdicted. The failures experienced in α-silyl radical investigations may now be more securely blamed upon back-bonding and steric factors.

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(8) (a) Silane 7 was identical with a sample prepared by the method of Kumada and coworkers:[8] H. Sakurai, A. Hosami, and M. Kumada, *Tetrahedron Lett.*, 1757 (1969).

(9) The properties of 8 corresponded to those reported by V. D. Tyurin, N. U. Ushakov, S. D. Gubin, and N. S. Nametkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1407 (1968).

(10) This is the third radical process that gave no rearrangement in α-silyl radical species. Earlier studies involved decarbonylation of an aldehyde[1] and decomposition of organometallics in the presence of transition metal ions.[1,2]

(11) Analogous phenyl shifts in organic systems are well known; *cf.* S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 138 (1956).

(12) See Kumada, *et al.*[8]

(13) In our case 7· is trapped out by the tin hydride. In Kumada's case, 7· would have a longer lifetime (hence it could cyclize) because chain transfer with silane 7 is an identity reaction. Kumada's group looked for the rearrangement to 4· but did not oberve it from 7·

(14) H. Sakurai, A. Hosomi, and M. Kumada, *Chem. Commun.*, 521 (1969).

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Photolysis of *N*-Alkoxy Quaternary Ammonium Salts. A Potential New Method of Aromatic Methoxylation

Sir:

The photochemistry of heterocyclic tertiary amine *N*-oxides has been the subject of extensive investiga-