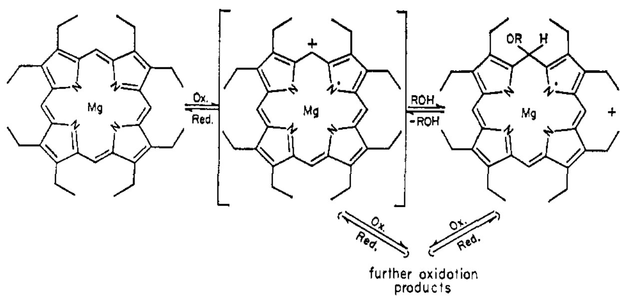

Figure 2.

phyrin. However, the initial part of the oxidation shows a ratio of 1.7 ± 0.3 mol of magnesium porphyrin to 1 mol of iodine. In agreement with this one-electron oxidation, the solution shows an esr spectrum of a single (Gaussian) line of width 4.9 ± 0.1 G and a g value of 2.0026 ± 0.0001. The line width and shape were invariant over a 100-fold range of concentration (10^{-5}–10^{-3} M). Calibration of the esr spectrometer with diphenylpicrylhydrazyl in the same solvent showed that 100 ± 30% of the green product could be accounted for as free radical. Moreover, the correlation of spins and absorbancies at 683 nm on titration with iodine was constant to ±20%, again over a 100-fold range. The esr signal also decreased or vanished on reversal of the reaction with KI or triethylamine.

Essentially the same product is obtained with dichlorodicyanobenzoquinone, bromine, N-bromsuccinimide, ferric chloride, and ferric perchlorate as oxidants of magnesium octaethylporphyrin in methanol. Oxidation with potassium permanganate, ceric sulfate, and sodium periodate gave the product absorbing at 683 nm, together with other products. No reaction occurred with p-benzoquinone or chloranil.

The formation of the green product stable for several hours occurs only in methanol and ethanol, and to some extent in 1-propanol with iodine as oxidant. No products absorbing beyond 620 nm are found in pyridine, chloroform, benzene, dimethyl sulfoxide, dimethylformamide, or petroleum ether. With bromine or N-bromsuccinimide in methanol as oxidant, a peak near 680 nm is observed in chloroform, dimethyl sulfoxide, dimethylformamide, 1- and 2-propanol, 1- and 2-butanol, and 2-methyl-1-propanol. In 2-methyl-2-propanol the absorption peak is at 640 nm. In all these cases the green color vanishes rapidly, yielding brown solutions with complex spectra.

The above properties are best explained by the reaction scheme given in Figure 2.

The formulation of the radical as a phlorin derivative follows from its absorption spectrum and its stability in simple alcoholic solvents. Some evidence for a cationic form, either the porphyrin radical shown or the fully oxidized species, was obtained by observing the cathodic migration of the green product on paper electrophoresis.

Zinc octaethylporphin is not oxidized under these conditions by iodine, but is by bromine. The main oxidation product here has a broad absorption band at 960 nm and is now under more detailed study. The free base and the copper derivative are yet more difficult to oxidize.

The facile oxidation of the magnesium porphyrin as compared with the zinc derivative may help explain why it is the former chelate which occurs in photosynthetic systems. We explain this effect by noting that the spectra indicate the magnesium chelate to be more ionic than that with zinc. We would expect the dianion of the porphyrin to be more readily oxidized; Fischer has shown[7] that porphyrin disodium salts are easily photooxidized.

This class of porphyrin oxidation product may be of interest not only as the first step in the biosynthesis of bile pigments but also for its relation to the radical observed in photosynthetic systems.[8] The radical discussed in this note has a g value the same as that observed in photosynthetic bacteria and similar to that observed in porphyrin and bacteriochlorophyll radicals.[9]

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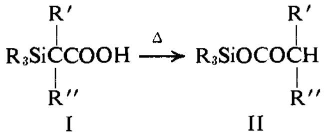
Thermal and Base-Catalyzed Rearrangements of Silylacetic Acids

Sir:

We wish to report that silylacetic acids (β-carboxysilanes), I, undergo thermal rearrangements to the isomeric acyloxysilanes (silyl esters), II, at or above their melting points when heated in sealed Pyrex tubes.



$$\underset{\text{I}}{R_3Si\overset{R'}{\underset{R''}{C}}COOH} \xrightarrow{\Delta} \underset{\text{II}}{R_3SiOCO\overset{R'}{\underset{R''}{C}}H}$$

I II

Related thermal rearrangements have been reported recently for β-keto silanes.[1] Data for the rearrangements of the silylacetic acids are given in Table I.[2]

When base is present, similar rearrangements occur at much lower temperatures, and under some circumstances the silylacyloxysilane, III, accompanies the simpler rearrangement product, II. Compound III, which may arise by attack of carboxylate ion on the rearrangement product, II, as shown, is generally observed in reactions run at high concentrations of acid I or base; the amount of III formed can usually be reduced, sometimes to negligible amounts, by working at low concentrations. Because of the possible complexity of these rearrange-

(1) A. G. Brook, D. M. MacRae, and W. W. Limburg, *J. Am. Chem. Soc.*, 89, 5493 (1967).

(2) Satisfactory analyses and spectra in complete accord with proposed structures have been obtained for all new compounds.

Table I. Thermal Rearrangements of Silylacetic Acids, $R_3SiCR'R''COOH$, in Sealed Pyrex Tubes

R	R′	R″	Temp, °C	Time	Product	Mp, °C	Yield, %
Ph	H	H	217	18 hr	$Ph_3SiOCOCH_3$	93–95	100[a]
Ph	H	Ph	170	17 hr	$Ph_3SiOCOCH_2Ph$	91–92	87[b,c]
			190	2½ hr	$Ph_3SiOCOCH_2Ph$	91–92	100[a,d]
Ph	H	CH_2Ph	217	19 hr	$Ph_3SiOCOCH_2CH_2Ph$	83.5–84.5	100[a]
Me	H	H	130	8 hr	$Me_3SiOCOCH_3$	*e*	10[f]
			134	7 days	$Me_3SiOCOCH_3$	*e*	84[g]

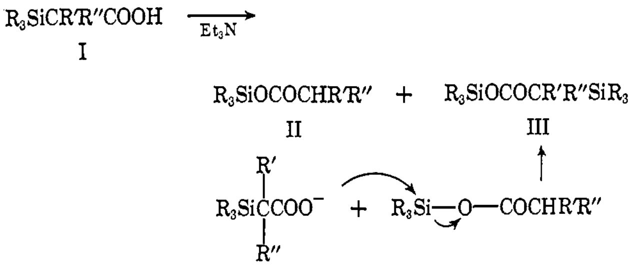
[a] Based on nmr spectroscopy. [b] Isolated recrystallized product. [c] In Pyrex glassware. [d] In a platinum dish. [e] Bp 102–103° (740 mm), n^{24}D 1.3823 (K. A. Andrianov and T. N. Ganina, *J. Gen. Chem. USSR*, **29**, 665, (1959), report n^{25}D 1.3810). [f] Identified by nmr. Also present were 50% starting material, 20% $Me_3SiOCOCH_2SiMe_3$ (bp 134° (36 mm) (Kugelrohr), n^{24}D 1.4148), and 20% HOAc. [g] Also present were 8% $Me_3SiOCOCH_2SiMe_3$ and HOAc.

Table II. Base-Catalyzed Rearrangements of Silylacetic Acids, $R_3SiCR'R''COOH$

R	R′	R″	Base[a]	Conditions	Product	Yield, %
Ph	H	Ph	0.06	25°, 4 hr, Et_2O	$Ph_3SiOCOCH_2Ph$	100[b] (80)[c]
			0.06	25°, 7 hr, C_6H_6	$Ph_3SiOCOCH_2Ph$	82[c]
Ph	H	CH_2Ph	0.04	85°, 17 hr, THF	$Ph_3SiOCOCH_2CH_2Ph$	70[c]
Ph	H	H	0.05	55°, 5 days, THF	No reaction	
Me	H	H	0.65	25°, 3 days, C_6H_6	$Me_3SiOCOCH_3$	65[d]
			0.04	25°, 14 days, C_6H_6	$Me_3SiOCOCH_3$	84[e]

[a] Mole equivalents of Et_3N per mole of acid. [b] Crude yield, estimated by nmr. [c] Isolated recrystallized material. [d] Nmr spectrum of crude product indicated in addition 35% $Me_3SiOCOCH_2SiMe_3$ and CH_3COOH. Materials were separated by glpc. [e] Nmr showed 16% unchanged acid as the only other component.

ments, we do not wish to comment further on their mechanisms at this time, particularly since both reactions have been found to occur much more rapidly than is suggested by the reaction times, given in Tables I and II, after which product yields were established. In fact, in some cases the reactions are probably complete in a matter of minutes, and the possibility that intermediates are formed is being investigated.



We have attempted to demonstrate that the thermal and base-catalyzed rearrangements are two distinct reactions by showing that the thermal reaction is not simply a reaction base catalyzed by the surface of the Pyrex reaction vessel. Thus triphenylsilylphenylacetic acid was readily rearranged at 190° in high yield in a platinum vessel specially treated to ensure the absence of base.

The carboxylic acids, some of which have been described before, were isolated by carbonation of the appropriate anions (prepared in a variety of ways to be described in a subsequent publication), followed by rapid work-up in the cold, avoiding basic conditions. Even under these very mild conditions, (triphenylsilyl)diphenylacetic acid could not be isolated. Instead (diphenylacetoxy)triphenylsilane, mp 104–105°, or its hydrolysis products, triphenylsilanol and diphenylacetic acid, were obtained.

With the discovery that these rearrangements occur readily, a number of observations in the literature may be explained. The decompositions reported for silylacetic acids, such as (triphenylsilyl)phenylacetic acid,[3] 9-(trimethylsilyl)-9-fluorenylcarboxylic acid,[4] and (trimethylsilyl)acetic acid,[5] to the related silanols (or disiloxanes) and carboxylic acids have been generally attributed to the facile displacement by base of CH_2COR groups from silicon. However, in basic medium, the silylacetic acids will actually be in the form of carboxylate ions and the implied displacement from silicon of a dianion would not be expected to occur easily. However, the formation of the observed products can be reasonably explained if the acids undergo the now-reported base-catalyzed isomerization to the acyloxysilanes, which subsequently undergo hydrolysis. The latter is well-known as a facile reaction.[6]

Further, Huang[7] has reported that carbonation of the Grignard reagent of triphenylchloromethylsilane gave triphenylsilylacetic acid, mp 92–93°. This is at variance with the value of 175–177° reported by Gilman[8] for the acid when prepared by oxidation of 2-triphenylsilylethanol and confirmed by ourselves[9] for acid prepared by carbonation of triphenylsilylmethyllithium. Since acetoxytriphenylsilane melts at 95°, it appears possibly that Huang, *et al.*, isomerized their acid, probably thermally, to the related acetoxysilane.

We are continuing our studies of these and related reactions.

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