# The Oxidation of Organosilanes with Selenium Dioxide

BY ROBERT A. BENKESER AND HERBERT LANDESMAN[1]

The action of strong oxidizing agents on organosilicon compounds leads to silicates and eventually silicon dioxide.[2] In fact the current analytical procedure for the quantitative determination of silicon in organosilanes consists in oxidizing these compounds to silicon dioxide with hot concentrated sulfuric acid,[3] a mixture of perchloric and nitric acids,[4] or sodium peroxide.[5] On the other hand, the effect of mild oxidizing agents on these compounds seems to have been studied in only one instance.[6] In the present research it was found that selenium dioxide oxidizes 2-acetyl-5-trimethylsilylthiophene[7] (I) and 2-acetyl-5-trimethylsilylfuran[7] to their corresponding glyoxals in 40–70% yields, without perceptible cleavage of the carbon–silicon bond.[8]

These glyoxals (e. g., II) formed hydrates (III), quinoxalines (V) and monosemicarbazones (IV).

As a further proof of structure, 2-(5-trimethylsilyl-2-thienyl)-quinoxaline (V) was also synthesized by the addition of 2-trimethylsilyl-5-thienyllithium[7] (VI) to the anil linkage of quinoxaline. The compound isolated was identical (mixed m. p.) with that obtained from the reaction between the glyoxal and o-phenylenediamine. The following equations summarize the reactions carried out with compound I
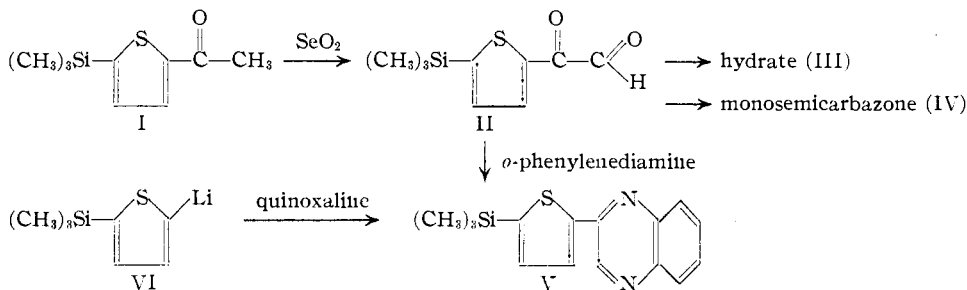
freshly sublimed selenium dioxide[9] in 100 ml. of commercial dioxane at 60°. The mixture was stirred at reflux for two and one-half hours, then cooled in ice and filtered by suction through a layer of Hyflo Supercel. The solvent was removed under reduced pressure (water pump) and the residual red oil, still containing some selenium, was distilled through a small Claisen head. The yield of pale yellow oil boiling at 89–90° (0.6 mm.) was 7.0 g. (73%). The oil darkens and solidifies on standing at room temperature under nitrogen.

A portion of the glyoxal was heated with ten times its volume of water and boiled with Norit after solution. The filtrate deposited white gelatinous flocs of the hydrate on cooling. After crystallization from dilute ethanol, it melted at 102–109°.[10]

Anal. Calcd. for $C_9H_{12}O_2Si \cdot H_2O$: C, 46.9; H, 6.08. Found: C, 46.7; H, 5.53.

The monosemicarbazone of this glyoxal can be prepared in the usual manner[11] from either the hydrate or the anhydrous oil. It melts at 221–224° (dec.).

Anal. Calcd. for $C_{10}H_{15}O_2N_3SSi$: C, 44.6; H, 5.57; N, 15.6. Found: C, 44.9; H, 5.52; N, 15.8.

2-(5-Trimethylsilyl-2-thienyl)-quinoxaline (Method A).—A solution of 0.2 g. (0.0008 mole) of (5-trimethylsilyl-2-thienyl)-glyoxal monohydrate in 20 ml. of 95% ethanol was added to a warm solution of 0.2 g. (0.0018 mole) of o-phenylenediamine in 20 ml. of 95% ethanol and the mixture was refluxed one hour. After standing overnight, water was added to precipitate the quinoxaline. After crystallization from dilute ethanol, there was obtained 0.2 g. (92%) of light yellow needles melting at 99–100°.[10]

Anal. Calcd. for $C_{15}H_{16}N_2SSi$: C, 63.3; H, 5.63; N, 9.86. Found: C, 63.0; H, 5.99; N, 9.64.

Essentially the same series of reactions was also successful with the corresponding furan compounds.

Experimental

(5-Trimethylsilyl-2-thienyl)-glyoxal Monohydrate.—Nine grams (0.046 mole) of 2-acetyl-5-trimethylsilylthiophene[7] was added to a solution of 5 g. (0.045 mole) of

(Method B).[12]—An ethereal solution of n-butyllithium[13] containing 0.056 mole of the organometallic was added under a nitrogen atmosphere to 9.4 g. (0.01 mole) of 2-thienyltrimethylsilane[7] dissolved in 50 ml. of anhydrous ether. The addition was made as rapidly as the evolved butane would allow. The mixture was refluxed three hours and was then added to 6.0 g. (0.05 mole) of quinoxaline[14] dissolved in 50 ml. of anhydrous ether. The dark solution was refluxed three hours and then allowed to stand overnight at room temperature. After hydrolysis with cold water, the ether layer was separated and dried

(1) Research Corporation Fellow.

(2) Friedel and Crafts, *Ann.*, **136**, 203 (1865).

(3) Kipping and Lloyd, *J. Chem. Soc.*, **79**, 449 (1901).

(4) Gilman, *et al.*, THIS JOURNAL, **68**, 2728 (1946).

(5) Marvin and Schumb, *ibid.*, **52**, 574 (1930).

(6) Vyle and Kipping [*J. Chem. Soc.*, **125**, 2616 (1924)] investigated the action of mercuric oxide on several organosilanes but obtained only complex mixtures as products.

(7) Benkeser and Currie, THIS JOURNAL, **70**, 1780 (1948).

(8) It is noteworthy that despite the instability of these ketones to acids, they were able to withstand the attack of selenious acid under the conditions of the experiment.

(9) Riley and Gray, "Organic Syntheses," Coll. Vol. II. John Wiley and Sons, Inc., New York, N. Y., 1943, p. 510.

(10) All melting points are uncorrected.

(11) Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 142.

(12) This experiment was run by Mr. Arnold Torkelson of these laboratories.

(13) Gilman, Zoellner and Selby, THIS JOURNAL, **55**, 1252 (1933).

(14) Cavagnol and Wiselogle, *ibid.*, **69**, 795 (1947).

over Drierite. After removal of the ether at atmospheric pressure, 10 ml. of nitrobenzene was added and the solution was refluxed twenty minutes. After removal of the nitrobenzene by distillation at reduced pressure the residue was taken up in dilute ethanol. This solution deposited dark red crystals after standing three days in a refrigerator. After six crystallizations from 95% ethanol 0.5 g. (4%) of pale yellow needles melting at 97.5–98° was obtained. A mixed melting point with the product obtained from Method A was not depressed.

5-Trimethylsilyl-2-furylglyoxal   Monohydrate.—Seven grams (0.064 mole) of freshly sublimed selenium dioxide[9] and 9 g. (0.064 mole) of 2-acetyl-5-trimethylsilylfuran[7] in aqueous dioxane were stirred at reflux for two hours. The mixture was worked up in a manner similar to that described for the thienylglyoxal. The yield of yellow oil boiling at 71° (0.6 mm.) was 5.0 g. (40%). This compound quickly darkens and solidifies on standing at room temperature under nitrogen.

A portion of the glyoxal was boiled with ten times its volume of water and the resulting solution was decolorized with Norit. The filtrate deposited white gelatinous flocs of the hydrate on cooling which melted at 108–114°[10] after crystallization from dilute ethanol.

Anal. Calcd. for $C_9H_{12}O_3Si\cdot H_2O$: C, 50.5; H, 6.5. Found: C, 50.6; H, 6.05.

2-(5-Trimethylsilyl-2-furyl)-quinoxaline.—This was prepared by Method A described for the corresponding thiophene derivative. It melted at 63–64°.

Anal. Calcd. for $C_{15}H_{16}ON_2Si$: C, 67.1; H, 6.0; N, 10.45. Found: C, 67.1; H, 6.2; N, 10.42, 10.68.

Summary

2-Acetyl-5-trimethylsilylthiophene and 2-acetyl-5-trimethylsilylfuran have been oxidized to the corresponding glyoxal by selenium dioxide. It is noteworthy that the silicon–carbon bond in these compounds was essentially unaffected by the oxidizing agent.

The glyoxals formed hydrates and quinoxaline derivatives. 2 - (5 - Trimethylsilyl - 2 - thienyl)-quinoxaline was also prepared in low yield by the addition of 5-trimethylsilyl-2-thienyllithium to the anil linkage of quinoxaline.

The Effect of Activator Concentration on the Infrared-sensitive Phosphor, Strontium Selenide–Samarium, Europium[1,2]

By Hilda Texin, Harry Williams[3] and Roland Ward

The brightness of the excited strontium sulfide–samarium, europium phosphor under constant infrared stimulation has been shown to be dependent upon the activator concentrations. Definite and reproducible maxima were observed in the curves relating the brightness with increasing concentrations of one activator, the concentration of the other activator being held constant.[4] Attempts to achieve similar results with the analogous strontium selenide phosphor were not immediately successful and for some time it was thought that there was an inherent difference in the selenide and sulfide phosphors. This paper describes some of the factors which influence the luminescent properties of the selenide phosphor and also gives an empirical method by which the brightness–activator concentration relationship can be established.

The preparation of strontium selenide for use as a phosphor material has been described.[5] In the experimental work reported here, strontium chloride was used as the flux in the conversion of the selenide to the phosphor. It was found that constant brightness values were obtained when the phosphor mixtures were heated at 1050° for one hour or longer. Some modifications were made in the procedure for the preparation of strontium selenide and, perhaps as a result of these improvements, it was no longer found necessary to add any sulfide to produce a sensitive phosphor.

Experimental

In all of this work we have had to depend upon making reproducible samples of the phosphor from a specific sample of strontium selenide. The solid ingredients of the phosphors were weighed and mixed in a dry-box but were exposed to the atmosphere of the laboratory for a short time during the molding of the sample. The reproducibility was usually within about 5%.

It has already been pointed out[5] that samples of strontium selenide prepared at different times frequently showed differences in brightness, time lag[5a] and phosphorescence. While it was suspected that most of these differences were due to the presence of varying amounts of oxide in the final phosphor, a search was made for other con-

(1) This work was performed under Contract NObsr 39045 of the Bureau of Ships with the Polytechnic Institute of Brooklyn.

(2) Abstracted in part from a thesis submitted to the Graduate School of the Polytechnic Institute of Brooklyn by H. Williams in partial fulfillment of the requirements for the degree of Master of Science, 1948.

(3) Present address: Chemistry Division, Naval Ordnance Test Station, Inyokern, Cal.

(4) K. F. Stripp and R. Ward, This Journal, **70**, 401 (1948).

(5) A. L. Smith, R. D. Rosenstein and R. Ward, *ibid.*, **69**, 1725 (1947).

(5a) "Time Lag" is an expression for the number of seconds that elapse between the time that the stimulating infrared light is turned on the phosphor until the brightness of the phosphor reaches maximum intensity. It decreases with increasing intensity of the infrared radiation.