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SILICON HETEROCYCLIC COMPOUNDS

III *. A 3-SILAOXETANE

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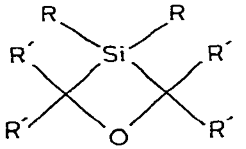
Summary

Synthesis of 3,3-dimethyl-2,2,4,4-tetraphenyl-3-silaoxetane, a new heterocyclic system, was accomplished in good yield. Its fluorescence spectrum may be evidence for transannular electronic interaction between oxygen and silicon.

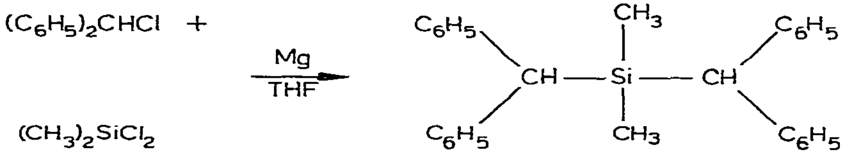
Many cyclic compounds are known that contain one or more Si—Z—C units where Z is usually O, N or S. However, to our knowledge there has been no previous report on a 3-silaoxetane (I) which contains the Si—C—O sequence in a small ring, although some recent reports [1—5] have given 2-silaoxetanes as reaction intermediates.



$R = CH_3$
and
$R' = C_6H_5$

(I)

Compound I can be prepared in good yield by a 3 step procedure.



(II)

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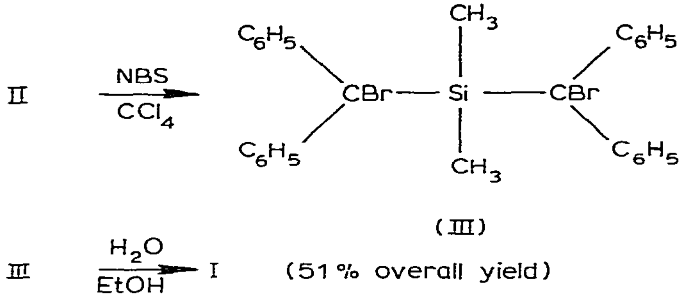
* For part II see ref. 9.



The symmetry of I and the lack of protons on the ring itself made identification via NMR or IR spectra difficult. The spectra were simple ones and consistent with the silaoxetane structure. The somewhat broad aromatic proton peak in the NMR may reflect ring bending or crowding of the phenyl groups, giving several environmental possibilities to the aromatic protons.

In the mass spectrum, beside the parent peak at *m/e* 406, the peak of next highest mass number was one at 332. This corresponds to the mass of tetraphenylethylene. The latter may arise through some thermal decomposition at the heated inlet (>200° C). Thermal decomposition experiments on 3,3-dimethyl-2,2,4,4-tetraphenyl-3-silaoxetane showed that decomposition was not significant up to 208° C but that at higher temperatures (up to 340° C) tetraphenylethylene was produced along with color changes in the sample and a sticky material with the composition and IR spectrum of $-(CH_3)_2SiO-$.

A saturated solution of the silaoxetane in acetone appeared visibly fluorescent. The fluorescence spectrum shows several peaks with fluorescence extending into the visible region.

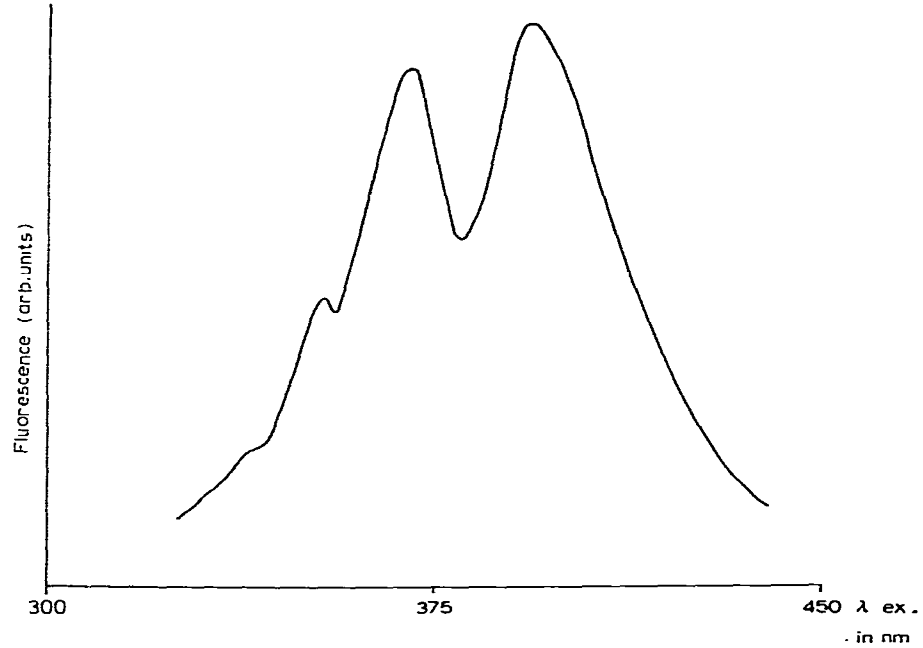


Fig. 1. Fluorescence exitation spectrum of 3,3-dimethyl-2,2,4,4-tetraphenyl-3-silaoxetane.

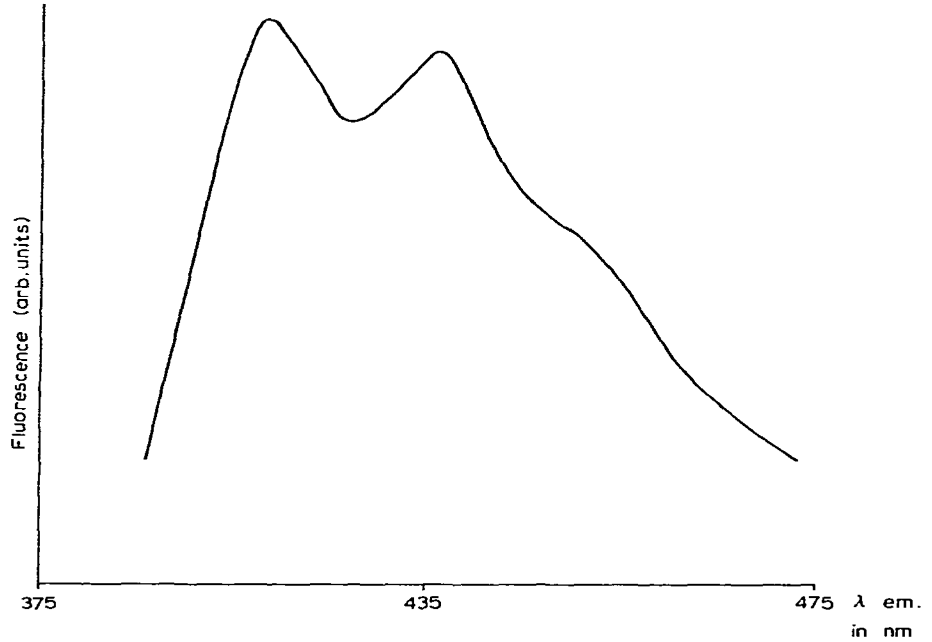


Fig. 2. Fluorescence emission spectrum of 3,3-dimethyl-2,2,4,4-tetraphenyl-3-silaoxetane.

Excitation was at 373 nm with band widths set at 5, 2.5, 2.5 and 5 nm of a 2.49×10^{-3} *M* solution of silaoxetane in heptane using a 1 cm cuvette (Fig. 1). Emission was monitored at 430 nm using the same cuvette size, band width settings and solution as above (Fig. 2). The analogous compound II without the silaoxetane ring was nearly inactive in fluorescence measurements over similar wavelengths.

Brook [6] has shown that α-ketosilanes also show some unusual electronic properties in that they exhibit remarkably strong n—π^* carbonyl absorptions at long wavelengths (420—440 nm for $R_3SiCOPh$). This has been attributed to the strong inductive effect (+*I*) of silicon at the ground state as well as π^* excited state interaction with silicon by back donation [7].

In the 3-silaoxetane system hyperconjugation effects such as reviewed by Pitt [8] are likely to be important as well since the ring structure imposes some stereoelectronic requirements. The Si—CH_3 bonds are thus probably in the same plane as one pair of n-electrons on oxygen leading to σ—n conjugation.

Preparation of the simpler 3-silaoxetane where R′ = H and the synthesis of other heteroatom analogs is currently underway.

Experimental

All melting points are uncorrected. The NMR spectra were obtained on a Varian A-60 Spectrometer with chemical shifts reported in δ (ppm) units relative to tetramethylsilane. Infrared spectra were determined on a Perkin-Elmer 457 Spectrophotometer and fluorescence work was done on a Farrand Mark I Spectrofluorimeter. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona.

Bis-(diphenylmethyl)-dimethylsilane (II)

To a large excess of magnesium turnings (36 g), 1.5 g-atom) and 400 ml of dry tetrahydrofuran in a 3 l flask was added 19.4 g (0.15 mol) of dichlorodimethylsilane. A dropping funnel was arranged so that addition was to a 10 ml pool of THF returning from the reflux condenser insuring high dilution of added reagents. A solution of 91.0 g (0.45 mol) of chlorodiphenylmethane and 18.90 g (0.1 mol) of 1,2-dibromoethane in 600 ml of dry THF was placed in the dropping funnel and addition of this solution over a 24 h period to the refluxing reaction mixture prevented much of the unwanted coupling product (1,1,2,2-tetraphenylethane) formation. Reflux was continued for 2 h after addition was complete. The solution was cooled, filtered and hydrolyzed by pouring into an equal volume of cold acidified water. Ether (500 ml) was added and the water layer and organic layer were separated. The water layer was then extracted with two 100 ml portions of ether and the combined ether extracts were dried over anhydrous $CaCl_2$. The mixed solvents were removed on a rotary evaporator and the residue was mixed with 500 ml of ether, cooled and filtered to remove most of the tetraphenylethane. Fraction crystallization from the ether solution produced 41.2 g (70% yield) of bis(diphenylmethyl)dimethylsilane: m.p. 105—106°C; IR (thin film) 1255 cm^{-1} ($Si—CH_3$); NMR (CCl_4) δ 0.08 (s, 6, $SiCH_3$). 3.41 (s, 2, CH) and 7.05 ppm (s, 20, arom.). (Found: C, 85.69; H, 7.24, $C_{28}H_{28}Si$ calcd: C, 85.61; H, 7.15%.)

Bis(bromodiphenylmethyl)dimethylsilane (III)

A 1 l flask was fitted with a reflux condenser and 39.2 g (0.1 mol) of bis-(diphenylmethyl)dimethylsilane, 35.6 g (0.2 mol) of *N*-bromosuccinimide and 400 ml of CCl_4 were added. The contents were refluxed for 4 h with 0.1 g of benzoyl peroxide added at the beginning and again after 2 h refluxing. After cooling, the succinimide was filtered off and then the CCl_4 was evaporated off. The residue was recrystallized from ether and yielded 42 g (74% yield) of product: m.p. 134—135°C; IR (thin film) 1260 cm^{-1} ($Si—CH_3$); NMR (CCl_4) δ 0.95 (s, 6, $SiCH_3$) and 6.97 ppm (s, 20, arom.). (Found: C, 61.11; H, 4.75. $C_{28}H_{26}Br_2Si$ calcd: C, 61.09; H, 4.73%.)

3,3-Dimethyl-2,2,4,4-tetraphenyl-3-silaoxetane (I)

In a 100 ml flask 5.50 g (0.01 mol) of bis-(bromodiphenylmethyl)dimethylsilane and 50 ml of 95% ethanol were refluxed for 2 h. After cooling the product was collected by filtration to give 4.0 g (98%): m.p. 198—200°C; IR (thin film) 1260 ($Si—CH_3$) and 955 cm^{-1} (C—O—C); NMR (CCl_4) δ 0.22 (s, 6, $SiCH_3$) and 6.83—7.35 ppm (m, 20, arom.); mass spec. parent at m/e = 406. (Found: C, 82.72; H, 6.50. $C_{28}H_{26}OSi$; calcd: C, 82.76; H, 6.44%.)

A sample recrystallization from acetone was used for the fluorescence spectrum (see discussion).

Thermal decomposition of 3,3-dimethyl-2,2,4,4-tetraphenyl-3-silaoxetane

Into a sublimation apparatus was placed 0.5 g (0.001 mol) of 3,3-dimethyl-2,2,4,4-tetraphenyl-3-silaoxetane. Heating on a sand bath caused the colorless crystals to decompose at 212—218°C, with the emission of vapors that eventually condensed on the cold finger of the apparatus. A sample removed at

208°C showed no decomposition by NMR analysis ($CDCl_3$) δ 0.70 (s, 6, Si—CH_3), 7.05—7.55 ppm (m, 20, arom.). As the temperature increased the viscous liquid change to yellow at 212—218°C; then orange at 230—250°C and finally to violet above 250°C. After heating to 340°C, the residue gave an NMR ($CDCl_3$) signal at δ 7.00—7.10 ppm (s, 20, arom.) as expected for tetraphenylethylene (also identified by mixed melting point). The sublimate IR, (KBr pellet) indicated the presence of —$Si(CH_3)_2O$—.

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