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SYNTHESIS AND REACTIONS OF THE CYCLIC SILYL PEROXIDE 1,1,4,4-TETRAMETHYL-2,3-DIOXA-1,4-DISILACYCLOHEXANE

Waldemar Adam* and Rainer Albert

Institute of Organic Chemistry, University of Würzburg, Am Hubland,
D-8700 Würzburg, Germany

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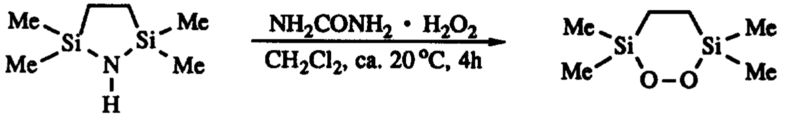
Abstract: *The first simple cyclic silyl peroxide, namely 1,1,4,4,-tetramethyl-1,4-disila-2,3-dioxane (1), was prepared by classical synthetic methodology from its corresponding cyclic disilazane and the urea complex of hydrogen peroxide.*

Carboxylic peroxides are long known and have been extensively employed in mechanistic and preparative applications. 1) This also is valid for acyclic silyl peroxides, particularly the recently much used *bis*(trimethylsilyl) peroxide, which as protected H_2O_2 exhibits marked advantages as oxidizing agent compared to the parent hydrogen peroxide. 2)

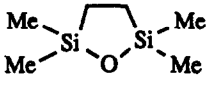
To date only a few cyclic silyl peroxide have been reported, 3) for which in view of the unconventional synthesis sterically large groups had to be utilized for persistence of these presumably labile peroxides. In contrast, we report herein the classical preparation of the first simple cyclic silyl peroxide, namely the novel 1,2-dioxane 1,1,4,4- tetramethyl-2,3-dioxa-1,4-disilacyclohexane (1). The synthetic strategy is based on the recently reported convenient preparation of *bis*(trimethylsilyl) peroxide, in which the hydrogen peroxide urea complex was treated with the silylated urea. 4) Unfortunately, we were unsuccessful in preparing the hitherto unknown urea derivative of 1,2-*bis*(chloromethylsilyl)ethane, but reaction of the readily available cyclic disilazane 5) directly with $NH_2CONH_2 \cdot H_2O_2$ afforded the desired disiladioxane 1 in 68 % yield, as colorless liquid, bp 68-69 °C/35 Torr; the peroxide titer (by iodometry) was 97 ± 0.8%. 6)



1 (68%)

Eq. 1

Modelled on classical, preparative peroxide chemistry, 1 i.e. nucleophilic substitution at the eletrophilic silicon atom, the synthetic pathway in Eq. 1 represents a novel variant, which allows for the first time convenient access to simple (not protected by sterically large substituents) cyclic silyl peroxides. That this is not necessarily obvious, was manifested by our numerous failures to functionalize directly the 1,2-*bis*(chlorodimethylsilyl)ethane with hydrogen peroxide to the desired disiladioxane 1). In these attempts, besides the cyclic disiloxane **2** and



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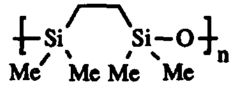

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the nonperoxidic polymer **3** (heating of the latter at 250 °C with KOH led to disiloxane **2** in 57% isolated yield 7), only small amounts of the disiladioxane **1** were spectroscopically detected. Efforts to obtain the cyclic silyl peroxide **1** by distillation or low temperature column chromatography (silica gel) of the complex product mixture failed in view of complete decomposition of the seemingly labile **1**. It should be mentioned that the reaction of the cyclic disilazane directly with H_2O_2 was also unsuccessful.

The above observations indicate a rather sensitive chemical behaviour of the new cyclic silyl peroxide **1**. Indeed, the latter is readily hydrolyzed to the nonperoxidic polymer **3**; also exposure to elevated temperatures induces such decomposition. When the cyclic silyl peroxide **1** was treated with a stoichiometric amount of triphenylphosphine in petroleum ether at 20 °C, deoxygenation (quantitative formation of triphenylphosphine oxide) afforded the cyclic disiloxane **2**, which was isolated by distillation in 57% yield as a colorless liquid (bp 125 °C /700 Torr) 8). With stoichiometric quantities of dimethyl sulfide in petroleum ether, the silyl peroxide **1** reacted slowly (ca. 12 h) even at 50 °C to afford 19% dimethyl sulfoxide, 15% dimethyl sulfone and ca. 50% polymer **3**, as observed by ^{1}H NMR spectroscopy directly on the reaction mixure.

These results confirm that the novel disiladioxane **1** serves as moderate oxygen transfer reagent.With the appropriate electrophilic activation, such novel *simple* cyclic silyl peroxides might serve as useful mild and selective oxidants. Be this as it may, we wish to stress that our *conventional* synthetic methodology obviates the dressing-up of the cyclic silyl peroxides with sterically demanding substituents on the silicon atoms for their stabilization and thereby not encumber their potential utility as oxygen transfer agents.

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6. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ= 0.20 (s, 12 H, CH_3), 0.82 (s, 4 H, CH_2).- ^{13}C-NMR ($CDCl_3$), 63 MHz): δ = -2.81 (q, CH_3), 6.73 (t, CH_2).- ^{29} Si-NMR ($CDCl_3$, 90 MHz): δ = 28.1 (s).-
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