# Brief Communications

## Synthesis of 2,2,6,6-tetramethyl-1-oxyl-4-piperidyloxy-*tert*-butylperoxyalkylsilanes

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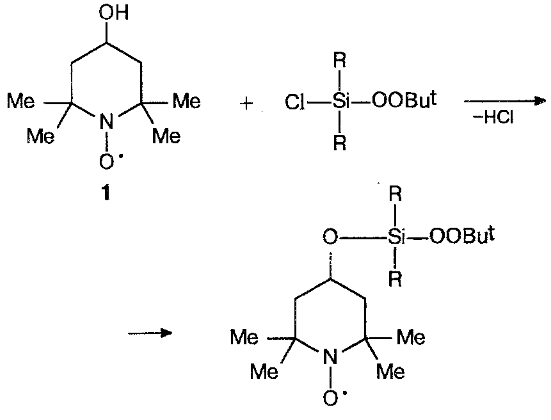
2,2,6,6-Tetramethyl-1-oxyl-4-piperidyloxy-*tert*-butylperoxyalkylsilanes were obtained by condensation of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl with organosilicon chloroperoxides $ClR_2SiOOR'$ (R = Me, Et; R' = $Bu^t$) in ether at 0—5 °C in the presence of a tertiary amine as an HCl acceptor.

**Key words**: 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl, organosilicon chloroperoxides, condensation; 2,2,6,6-tetramethyl-1-oxyl-4-piperidyloxy-*tert*-butylperoxyalkylsilanes.

In recent years, considerable attention has been attracted by peroxides containing various functional groups, which can be introduced into peroxide molecules in order to control their solubility in media with various polarities and to enhance their stability in storage, their resistance against mechanical impact, and their sensitivity to heating. Introduction of functional groups makes it possible to convert the usual peroxide ingredients of polymerization or vulcanization into peroxide reagents.

The purpose of the present work was to obtain 2,2,6,6-tetramethyl-1-oxyl-4-piperidyloxy-*tert*-butylperoxyalkylsilanes by condensation of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl (**1**) with organosilicon peroxides $ClR_2SiOOR'$ (where R = Me, Et; R' = $Bu^t$) in an inert organic solvent at 0—5 °C in the presence of a tertiary amine as an HCl acceptor (Scheme 1).

**Scheme 1**



**2**: R = Me (**a**), Et (**b**) **2a,b**

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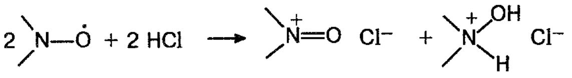
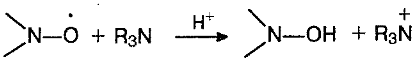
The HCl liberated in this reaction not only shifts the equilibrium towards the starting reagents but also reacts with the nitroxyl group.[1]



The presence of a nitroxyl group along with a hydroxyl group in compound **1** significantly restricts the choice of an HCl acceptor, since tertiary amines can reduce nitroxyl radicals.[2]



The transfer of an electron from the amine to the nitroxyl radical occurs particularly readily in an acid medium; hence the HCl formed catalyzes the reaction. Therefore, pyridine or trialkylamines, which do not react with nitroxyl radicals and effectively bind HCl, can be used as acceptors. The resulting quaternary salts of these amines have low oxidative potentials and can be reduced only by very strong reducing agents; hence the reaction between pyridinium chloride and the nitroxyl radical does not occur. In order to avoid hydrolysis of amine salts yielding HCl, dry amines should be used. It should also be noted that the reaction products react with HCl at high temperatures, which is responsible for their intense resinification.

Thus, the optimum conditions for the reaction studied (see Scheme 1) include excess triethylamine or pyridine and low temperature.

## Experimental

IR spectra were recorded on a UR-20 spectrometer.

**2,2,6,6-Tetramethyl-1-oxyl-4-piperidyloxy-*tert*-butylperoxydimethylsilane (2a).** *tert*-Butylperoxydimethylchlorosilane [$Me_3COOSiMe_2Cl$, b.p. 30 °C (15 Torr), $d_4^{20}$ 0.9613, $n_D^{20}$ 1.4082; found (%): O, 8.75; Cl, 19.35] (3.2 g, 0.00174 mol) in dry ether (20 mL) was added dropwise with stirring at 0 °C over a period of 30 min to a solution of compound **1** (3 g, 0.00174 mol; orange rhombic crystals, m.p. 71.5 °C)[3] and pyridine (1.4 g) in dry ether (50 mL). The reaction mixture was gradually heated to 20 °C and stirred for an additional 4 h. The precipitate of pyridinium chloride (1.98 g, 98.5 %) was filtered off in the absence of moisture, and the filtrate was concentrated *in vacuo*. The remaining volatile products were distilled off for 60 min at 45—50 °C (0.5—1 Torr) to give 5.1 g (yield 92 %) of an orange-red oily liquid containing (according to iodometric data) 98 % of product **2a**: $d_4^{20}$ 0.9743, $n_D^{20}$ 1.4463. Found (%): C, 56.93; H, 10.39; N, 4.32; Si, 8.58. $C_{15}H_{32}NO_4Si$. Calculated (%): C, 56.56; H, 10.13; N, 4.40; Si, 8.82. IR, ν/cm$^{-1}$: 1360 (>N—O$^\cdot$); 1085 (SiO); 1260 (Me in $SiMe_2$); 880 and 1200 (Me in $CMe_3$); 916 (O—O).

**2,2,6,6-Tetramethyl-1-oxyl-4-piperidyloxy-*tert*-butylperoxydiethylsilane (2b).** The reaction of compound **1** (3 g) with *tert*-butylperoxydiethylchlorosilane [$Me_3COOSiEt_2Cl$, b.p. 70 °C (15 Torr), $d_4^{20}$ 0.9952, $n_D^{20}$ 1.4321; found (%): O, 7.6; Cl, 16.8] (3.7 g) was carried out under the conditions specified above to give 5.5 g (yield 91 %) of a red oily liquid containing (according to iodometric data) 98 % of product **2b**: $d_4^{20}$ 0.9664, $n_D^{20}$ 1.4500. Found (%): C, 58.65; H, 10.32; N, 3.95; Si, 7.90. $C_{17}H_{36}NO_4Si$. Calculated (%): C, 58.92; H, 10.47; N, 3.95; Si, 7.62. IR, ν/cm$^{-1}$: 1360 (>N—O$^\cdot$); 1093 (SiO); 1240 (Et in $SiEt_2$); 910 (O—O).

## References

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