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Abstract

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Chemistry

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SYNTHESIS OF UNSATURATED ORGANOSILICON PEROXIDES

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In a previous paper (ˆ1) we reported the preparation of unsaturated organosilicon peroxides of mixed type with an ethynyl radical at the Si atom, ≡ Si—OO—C ≡ C, and a vinyl radical at the Si atom, CH_2 = CH—SiR_m—[−OO—C(R)$_3$]$_n$, and with one, two, and three peroxide groups. Peroxides of this type are distinguished by increased thermal stability (decomp. temp. 150-170°) and therefore proved suitable for vulcanization processes and high-temperature polymerization. In order to develop studies on peroxides of this type, the present work describes the preparation of a series of unsaturated organosilicon peroxides that differ in the composition of the saturated and unsaturated radicals at the Si atom and at the tertiary C atom, while containing one and two peroxide groups in the molecule.

Preparation of mono-tert-amyl peroxyvinylmethylethylsilane CH_2 = CH—Si$(CH_3)(C_2H_5)$OOC$(CH_3)_2C_2H_5$. First, tert-amyl hydroperoxide was obtained by a known method (ˆ2) from tert-amyl alcohol (prepared by us by organomagnesium synthesis) and 30% hydrogen peroxide; it had the following characteristics: d_4^{20} 0.903; n_D^{20} 1.4163 (lit. value 1.4161); active oxygen found 15.3%, theoretical 15.35%. The starting vinylmethylethylchlorosilane was obtained by the interaction of vinylmethyldichlorosilane with ethylmagnesium bromide. Purification was carried out by rectification in vacuo, and its purity was checked by chlorine content: found 26.3% (theoretical 26.4%).

The peroxide was obtained as follows: to a solution cooled to −3° of 13.5 g (0.1 mole) of freshly distilled vinylmethylethylchlorosilane in 100 ml of petroleum ether (fraction up to 40°), a mixture of 10.4 g (0.1 mole) of tert-amyl hydroperoxide and 7.9 g (0.1 mole) of pyridine in 50 ml of petroleum ether was added dropwise. The reaction temperature was maintained not above 0° with vigorous stirring. Then, after the reaction mixture had stood for 3 hours at room temperature, the pyridine hydrochloride was dissolved in a small amount of water and separated. The organic layer was washed with water, dried over magnesium

sulfate, and subjected to distillation in vacuo. First, at room temperature under the vacuum of a water-jet pump the solvent was distilled off, and then the peroxide was distilled on a water bath. At a residual pressure of 1–2 mm and 38°, a fraction was collected in the amount of 12 g, corresponding to a yield of 59%. The obtained peroxide fraction was then distilled again. The synthesized peroxide is a liquid with a faint camphor odor and has the following characteristics: n_D^{20} 1.4308, d_4^{20} 0.8763; molecular weight found (cryoscopically in benzene) 197.8, calculated 202.38; MR found 59.53, calculated 60.61.

$C_{10}H_{22}SiO_2$.	Found %:	C 59.53; H 11.11; Si 14.02
	Calculated %:	C 59.35; H 10.96; Si 13.88

Iodometrically, active oxygen was found to be 7.9% (theoretical 7.9%).

The structure of tert-amyl peroxyvinylmethylethylsilane was confirmed by hydrolysis in the presence of hydrochloric acid. From the hydrolysis products, tert-amyl hydroperoxide and vinylmethylethylsilanol were isolated. Reduction-

with potassium iodide in an acidic medium or with sodium thiosulfate in a neutral medium [1], tert-amyl alcohol and vinylethylsilanol were obtained.

Preparation of monocumyl vinylmethylethylsilane peroxide CH_2=CH—Si(CH_3)(C_2H_5)OOC(CH_3)$_2$$C_6H_5$. The starting cumene hydroperoxide was prepared [3] from technical (70%) material through the sodium salt, followed by vacuum distillation (0.1 mm Hg); the fraction at 52–53° was collected and had the following characteristics: n_D^{20} 1.5232 (literature value 1.5233); active oxygen content 10.5% (theoretical 10.5%). The peroxide was synthesized by the method described above from 13.5 g of freshly redistilled vinylmethylethylchlorosilane and 15.2 g of cumene hydroperoxide in the presence of 7.9 g of pyridine. Because of the closeness of the boiling points of the initial hydroperoxide and the synthesized peroxide, the latter was subjected to double vacuum distillation, and a fraction was collected at 55° (0.1 mm); 10.8 g of peroxide was obtained (yield 43%). The synthesized peroxide was an oily liquid with the following characteristics: n_D^{20} 1.4910; d_4^{20} 0.9656; molecular weight found 243.8, calculated 250.42; MR found 75.11, calculated 75.29.

$C_{14}H_{22}SiO_2$.	Found %:	C 67.00;	H 8.87;	Si 11.48
	Calculated %:	C 67.15;	H 8.86;	Si 11.22

Active oxygen found 6.3% (theoretical 6.4%).

Preparation of di-tert-butyl vinylpropylsilane peroxide CH_2=CH—Si(C_3H_7)[—OO—C(CH_3)$_3$]$_2$. The starting vinylpropyldichlorosilane was prepared by organomagnesium synthesis from vinyltrichlorosilane and propylmagnesium bromide; b.p. 147°, chlorine content 42.15% (theoretical 41.93%).

The peroxide was synthesized by reaction of 33.8 g of vinylpropyldichlorosilane with 36.1 g of tert-butyl hydroperoxide and 31.7 g of pyridine. Fractional vacuum distillation gave a peroxide fraction at 76° (1–1.5 mm) in an amount of 25 g (yield 45%), having the following characteristics: n_D^{20} 1.4269; d_4^{20} 0.9054; molecular weight found 263.8, calculated 276.46; MR found 78.25, calculated 77.57.

$C_{13}H_{28}SiO_4$.	Found %:	C 56.80;	H 10.40;	Si 10.42
	Calculated %:	C 56.48;	H 10.21;	Si 10.16

Active oxygen found 11.55% (theoretical 11.6%).

Preparation of di-tert-amyl vinylmethylsilane peroxide $CH_2{=}CH{-}Si(CH_3)[{-}OO{-}C(CH_3)_2C_2H_5]_2$. This peroxide was synthesized by reaction of 14.1 g of vinylmethyldichlorosilane with 20.8 g of tert-amyl hydroperoxide in the presence of 15.8 g of pyridine. Vacuum distillation gave a fraction with b.p. 62° (0.5–1 mm) in an amount of 15.9 g (yield 58%), having the following characteristics: n_D^{20} 1.4312; d_4^{20} 0.9228; molecular weight found 264.1, calculated 276.46; MR found 77.58, calculated 77.57.

$C_{13}H_{28}SiO_4$.	Found %:	C 56.51;	H 10.31;	Si 10.09
	Calculated %:	C 56.48;	H 10.21;	Si 10.16

Active oxygen found 11.5% (theoretical 11.6%).

Preparation of di-tert-amyl vinylpropylsilane peroxide $CH_2{=}CH{-}Si(C_3H_7)[{-}OO{-}C(CH_3)_2C_2H_5]_2$. The synthesis was carried out by reaction of 25.4 g of freshly redistilled vinylpropyldichlorosilane with 31.3 g of tert-amyl hydroperoxide and 23.7 g of pyridine. Vacuum distillation gave a peroxide fraction with b.p. 56° (0.05 mm) in an amount of 30 g (yield 66%), having the following characteristics: n_D^{20} 1.4359;

d_4^{20} 0.9145; molecular weight found 291.3, calculated 304.51; MR found 87.04, calculated 86.86.

$C_{15}H_{32}SiO_4$.	Found, %:	C 59.40;	H 10.79;	Si 9.42
	Calculated, %:	C 59.17;	H 10.59;	Si 9.23

Active oxygen found 10.3% (theoretical 10.5%).

Preparation of di-tert-butyl peroxyallylmethylsilane
$CH_2{=}CH{-}CH_2{-}Si(CH_3)[{-}OO{-}C(CH_3)_3]_2$. This peroxide was obtained by the interaction of tert-butyl hydroperoxide with allylmethyldichlorosilane in the presence of pyridine.

Allylmethyldichlorosilane was synthesized by the successive introduction of allyl and methyl groups into the molecule of silicon tetrachloride. Treatment

of silicon tetrachloride with an equimolecular amount of allylmagnesium bromide, followed by vacuum rectification on a column with nichrome spirals, gave allyltrichlorosilane with b.p. 115–118° (literature value 117.5°) and an active chlorine content of 60.9% (theoretical 60.6%). Then allylmethyldichlorosilane was obtained from allyltrichlorosilane and methylmagnesium iodide; b.p. 118–120° (literature value 120°), chlorine content 45.9% (theoretical 45.7%).

The peroxide was obtained by the interaction of 31.0 g of allylmethyldichlorosilane and 31.7 g of pyridine in petroleum ether. During vacuum distillation, a fraction with b.p. 31° (0.1 mm) was collected in an amount of 21.2 g (yield 40%). The peroxide obtained is a colorless liquid, fairly thermally stable: noticeable evolution of gas bubbles begins when it is heated to 158° and ends when the temperature reaches 191–192°.

Di-tert-butyl peroxyallylmethylsilane has the following characteristics: n_D^{20} 1.4182; d_4^{20} 0.9094; molecular weight found 252.1, calculated 262.40; MR found 72.75, calculated 72.92.

$C_{12}H_{26}SiO_4$.	Found, %:	C 54.85; H 9.88; Si 10.90
	Calculated, %:	C 54.93; H 9.66; Si 10.69

Active oxygen found 12.0% (theoretical 12.2%).

Along with the described diatomic peroxides, we attempted to obtain, in pure form, analogous peroxides with cumene hydroperoxide. However, during fractional distillation (0.01 mm) on a boiling water bath, these peroxides do not distill. Nor is it possible to isolate these peroxides by freezing them out of solution. In the synthesis, after removal of the solvent, these peroxides are obtained as concentrates containing 65–70% of the pure product. In this form they were tested in the vulcanization of rubber mixtures of various rubbers, and positive results were obtained.

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Note: Figure translations are in progress. See original paper for figures.