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Abstract

Full Text

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SYNTHESIS OF UNSATURATED ORGANOSILICON PEROXIDES

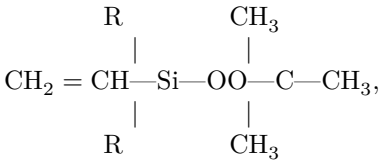
(Presented by Academician B. A. Arbuzov, 28 IX 1960)

Along with organic peroxide compounds, chemists have recently shown interest in various types of organosilicon peroxide compounds. The preparation of organosilicon peroxide compounds of the types $(R)_3Si—OO—Si(R)_3$ (I) and $(R)_3SiOOH$ (II) is first mentioned in Berry' s patent ([1]). Later, Bansel and Davies ([2,3]) described in detail a series of peroxides of the mixed type $(R)_3Si—OO—C(R)_3$ (III). In the work of Ghan and Metzinger ([4]), the preparation and characterization of these types of compounds are presented: the first two were synthesized mainly by the reaction of trialkyl- or triarylmonochlorosilanes with hydrogen peroxide or sodium peroxide, and the third type with alkyl hydroperoxides. Original methods were also used. Thus, in patent ([1]) the first type of peroxides is recommended to be obtained by the reaction of sodium monosilanolates with chlorine or bromine, and in the work of Pike and Shaffer ([5])—from tetraalkylsilanes through sulfates, with subsequent reaction of the sulfates with hydrogen peroxide. The third, mixed type was obtained by the same authors by the reaction of trialkylsilanamines with alkyl hydroperoxides.

Judging from the literature data, organosilicon peroxide compounds differ from organic ones in a number of features: lower thermal stability ([3,4]), a tendency toward rearrangements, as shown in the work of Bansel and Davies ([6]), and also by the character of the infrared spectra ([7]).

The authors ([3,4]) recommend using these compounds to initiate polymerization, and also as oxidizing agents.

From a review of the literature it is evident that unsaturated organosilicon peroxide compounds have not yet been synthesized and studied; it should be noted that organic unsaturated peroxide compounds also remain little studied. We set ourselves the task of synthesizing a series of unsaturated vinyl organosilicon peroxide compounds of the third mixed type, of the general formula



with one, two, and three peroxide groups.

Preparation of mono-tert-butyl peroxymethylvinylethylsilane

$$CH_2 = CH—Si(CH_3)(C_2H_5)OOC(CH_3)_3.$$

The starting methylvinylethyldichlorosilane was synthesized by us by the reaction of methylvinyldichlorosilane with ethylmagnesium bromide, with subsequent characterization of it by chlorine content, which was found to be 26.2% (theoretical 26.4%).

The synthesis of the peroxide was carried out as follows. To a solution, cooled to −3°, of 27 g of freshly distilled methylvinylethylchlorosilane in 150 ml of petroleum ether (b.p. up to 35°), with vigorous stirring, a mixture of 18 g of tert-butyl hydroperoxide (100%) and 15.8 g of pyridine in 50 ml of petroleum ether was added dropwise. The reaction proceeded vigorously, but the temperature of the reaction medium was kept no higher than 0°. After the addition and a subsequent 3-hour standing at room temperature, the precipitate of pyridine hydrochloride was removed with water; the organic layer was washed with water and dried over magnesium sulfate. Then, after removal of the ether, the peroxide was distilled in vacuo at 4 mm Hg and a boiling temperature of 31°. In all, 22 g of peroxide was obtained. The peroxide obtained was a transparent liquid with the following characteristics: n_D^{20} 1.4206; d_4^{20} 0.8565; σ_{20} 24.22 dyn/cm; mol. wt. (cryosc. in C_6H_6) 179, calcd. 188.32; MR 55.74, calcd. 55.96.

Found %: C 57.28; H 10.88; Si 14.83

$C_9H_{20}SiO_2$. Calculated %: C 57.40; H 10.70; Si 14.90

Active oxygen was determined by the iodometric method: found 8.4%, calculated 8.49%. Decomp. temp. 173°.

The structure of the synthesized peroxide was confirmed by its reduction: 5.8 g of peroxide was shaken for 6 hours at room temperature with 6 g of anhydrous sodium sulfite in 40 ml of water. After standing for 30 min, the upper layer was separated, dried, and subjected to distillation at atmospheric pressure. Three fractions were obtained: b.p. 75-82° ($n = 1.388$); 82-120° ($n = 1.395$) and 120-145° ($n = 1.429$). After redistillation of the last, a fraction with b.p. 134-136° (n_D^{20} 1.4321) was obtained, which we identified as methylvinylethylsilanol. In the distillation of the aqueous layer, tert-butyl alcohol was also isolated.

Preparation of di-tert-butyl peroxymethylvinylsilane

$$CH_2{=}CH{-}Si(CH_3)[{-}OO{-}C(CH_3)_3]_2.$$

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By the method described above, from 21.2 g of freshly distilled methylvinyldichlorosilane (d = 1.09, chlorine 50.3%, theor. 50.2%) and 27 g of tert-butyl hydroperoxide in the presence of 23.8 g of pyridine, 18.8 g of peroxide was obtained with b.p. 90-91° (20 mm Hg), at 79° (11 mm), and 41-42° (1 mm). The peroxide was a liquid with the following characteristics: n_D^{20} 1.4210; d_4^{20} 0.9206; σ 24.83 dyn/cm; mol. wt. 243.5, calcd. 248.37; MR 68.42, calcd. 68.27.

Found %: C 53.13; H 9.89; Si 11.41

$C_{11}H_{24}SiO_4$. Calculated %: C 53.19; H 9.74; Si 11.30

Active oxygen found 12.64%; calculated 12.88%. Decomp. temp. 150.5° (with explosion).

Preparation of di-tert-butyl peroxyvinylethylsilane

$$CH_2{=}CH{-}Si{-}(C_2H_5)[{-}OO{-}C(CH_3)_3]_2.$$

The starting vinylethyldichlorosilane was synthesized by us by the action of ethylmagnesium bromide on vinyltrichlorosilane in abs. ether. After isolation and distillation, vinylethyldichlorosilane was obtained with b.p. 123° and a chlorine content of 45.9% (theor. 45.7%).

Then, from 23.3 g of vinylethyldichlorosilane and 27 g of tert-butyl hydroperoxide in the presence of 23.8 g of pyridine, by the procedure described above, a peroxide was obtained, which distilled at b.p. 63° (2 mm). The peroxide obtained was a transparent liquid with the following characteristics: n_D^{20} 1.4241; d_4^{20} 0.9112; σ_{20} 25.75 dyn/cm; mol. wt. 256, calcd. 262.4.

Found %: C 54.75; H 9.88; Si 11.06

$C_{12}H_{26}SiO_4$. Calculated %: C 54.93; H 9.99; Si 10.69

MR 73.49; calculated 72.92; active oxygen content found 12.3%, calculated 12.19%. Decomposition temperature 159° (with explosion).

Preparation of vinylsilane tri-*tert*-butyl peroxide

$$CH_2{=}CH{-}Si[{-}OO{-}C(CH_3)_3]_3.$$

From 16.2 g of freshly distilled vinyltrichlorosilane (d = 1.27, chlorine 65.8%) and 27 g of *tert*-butyl hydroperoxide, in the presence of 23.8 g of pyridine, by the method described above, a peroxide was obtained which, on distillation in vacuo (with nitrogen passed through a capillary), distilled over at 75-80° (1 mm). On redistillation at the same residual pressure, a fraction with b.p. 78° was collected in an amount of 13 g. The peroxide obtained was a transparent liquid with the

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following characteristics: n_D^{20} 1.4237; d_4^{20} 0.9576; σ_{20} 25.96 dyn/cm; mol. wt. 317, calculated 322.57; MR 85.83; calculated 85.22.

$C_{14}H_{30}SiO_6$.	Found, %:	C 52.03; H 9.14; Si 8.68
	Calculated, %:	C 52.15; H 9.38; Si 8.70

Active oxygen found 14.2%, calculated 14.89%. Decomposition temperature 147.5° (with explosion).

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

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