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1965

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Abstract

Full Text

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SYNTHESIS AND PROPERTIES OF tert-BUTYL ESTER OF β-(TRIMETHYLSILYL)-PERPROPIONIC ACID

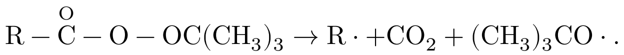
Recently the first organosilicon compounds with a peroxide group in the alkyl radical were obtained ([1,2]). By studying the homolytic decomposition of such substances, one can form an idea of the influence of the silicon atom on the properties of the free radicals containing it. In particular, the reactivity of the $(CH_3)_3SiCH_2CH_2CO_2\cdot$ and $(CH_3)_3SiCH_2CH_2\cdot$ radicals can apparently be judged by investigating the decomposition of tert-butyl ester of β-(trimethylsilyl)-perpropionic acid in various media. This perester was obtained by us in yields of up to 60% by the action of β-(trimethylsilyl)-propionyl chloride on the sodium salt of tert-butyl hydroperoxide. Its reactions with chlorobenzene, cumene, and tetraethyllead in the absence of oxygen proceed at an appreciable rate only at 126°, with formation of complex mixtures of products (Table 1). Judging from their composition, the primary act of the reactions is homolysis of the perester at the O–O bond. Some of the radicals formed then decompose according to equations (2) and (3)

$$(CH_3)_3SiCH_2CH_2COOOOC(CH_3)_3 \to (CH_3)_3SiCH_2CH_2CO_2\cdot + (CH_3)_3CO\cdot; \tag{1}$$

$$(CH_3)_3SiCH_2CH_2CO_2\cdot \to CO_2 + (CH_3)_3SiCH_2CH_2\cdot, \tag{2}$$

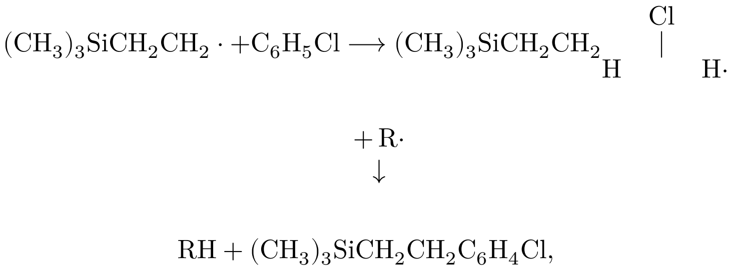
$$(CH_3)_3CO\cdot \to CH_3COCH_3 + CH_3\cdot\,. \tag{3}$$

As is known, for peracid esters an alternative decomposition mechanism is possible, with concerted rupture of two bonds simultaneously,



$$R - \overset{O}{C} - O - OC(CH_3)_3 \to R\cdot + CO_2 + (CH_3)_3CO\cdot\,.$$

But this mechanism is valid for peresters that give sufficiently stable R· radicals, such as benzyl ([3]), trichloromethyl ([3]), trimethylmethyl ([4]), or substituted benzyl (^{5}). In addition, such decomposition proceeds with practically quantitative yield of carbon dioxide, which is not the case here. Cumene, in interaction with radicals formed according to equations (1)–(3), is a hydrogen donor (Table 1, experiment 1). Along with tert-butanol, β-(trimethylsilyl)-propionic acid, trimethylethylsilane, and methane, secondary $C_6H_5C(CH_3)_2$ radicals are formed. They recombine to give dicumyl. Chlorobenzene cannot be a hydrogen donor in free-radical reactions (^{6}). However, in this solvent as well the perester decomposes with formation of tert-butanol, methane, β-(trimethylsilyl)-propionic acid, and trimethylethylsilane (Table 1, experiment 2). They may arise in the process of β-(trimethylsilyl)-ethylation of the chlorobenzene nuclei



$$(CH_3)_3SiCH_2CH_2\cdot + C_6H_5Cl \longrightarrow (CH_3)_3SiCH_2CH_2{}_{H}\ \overset{Cl}{|}\ {}_{H\cdot} \qquad (4)$$

$$\begin{array}{c} +\,R\cdot \\ \downarrow \end{array}$$

$$RH + (CH_3)_3SiCH_2CH_2C_6H_4Cl,$$

where

$$R = (CH_3)_3CO,\ CH_3,\ (CH_3)_3SiCH_2CH_2CO_2 \text{ and } (CH_3)_3SiCH_2CH_2.$$

Table 1

Reactions of tert-butyl β-(trimethylsilyl)perpropionate (I) with cumene (II), chlorobenzene (III), tetraethyltin (IV), and hexaethyldistannane (V) in the absence of atmospheric oxygen

Experiment No.	Taken into reaction, moles	Temperature, °C	Time, h	Reaction products*, moles per 1 mole of perester
1	0.0132 I0.550 II	126	7	0.60 CO_2; 0.42 CH_4; 0.60 $(CH_3)_3COH$0.40 $(CH_3)_2CO$; 0.45 $(CH_3)_3SiC_2H_5$0.33 $(CH_3)_3SiCH_2CH_2CO_2H$; 0.76 dicumyl
2	0.0128 I0.900 III	126	7	0.72 CO_2; 0.65 CH_4; 0.44 $(CH_3)_3COH$0.61 $(CH_3)_2CO$; 0.10 $(CH_3)_3SiC_2H_5$0.23 $(CH_3)_3SiCH_2CH_2CO_2H$0.20 $ClC_6H_4CH_2CH_2Si(CH_3)_3$; resin
3	0.0071 I0.130 IV	126–128	7	0.36 CO_2; traces of CH_4; 0.93 $(CH_3)_3COH$0.29 $(CH_3)_3SiC_2H_5$; 0.62 C_2H_4; 0.18 $C_2H_6$0.29 $(CH_3)_3SiCH_2CH_2CO_2H$0.42 $(C_2H_5)_3SnOCOCH_2CH_2Si(CH_3)_3$**
4	0.0045 I0.0045 V	100	2	0.70 $(C_2H_5)_3SnOC(CH_3)_3$; 0.03 $(CH_3)_3COH$0.93 $(C_2H_5)_3SnOCOCH_2CH_2Si(CH_3)_3$traces of $(CH_3)_2CO$ and CH_4

Notes. * The yield of CO_2 was determined from the gain in weight of absorbers filled with 30% KOH solution; gaseous hydrocarbons were analyzed by a chromatographic method; solid products were identified by the melting points of mixed samples with pure substances; the method of identification of other products is given in the experimental part.

** M.p. 89–90° (from heptane). Found, %: $(CH_3)_3SiCH_2CH_2CO_2$ 40.90. $C_{12}H_{28}O_2SnSi$. Calculated, %: $(CH_3)_3SiCH_2CH_2CO_2$ 41.36.

In accordance with the scheme, we isolated a fraction whose elemental analysis and IR spectrum correspond to β-(chlorophenyl)-ethyltrimethylsilane. Its yield (see Table 1) is much less than the total yield of tert-butanol, methane, and β-(trimethylsilyl)propionic acid. This contradicts scheme (4), according to which the yields of RH and $(CH_3)_3SiCH_2CH_2C_6H_4Cl$ should be equal. Consequently, the radicals $R\cdot$ are saturated with hydrogen not only according to scheme (4).

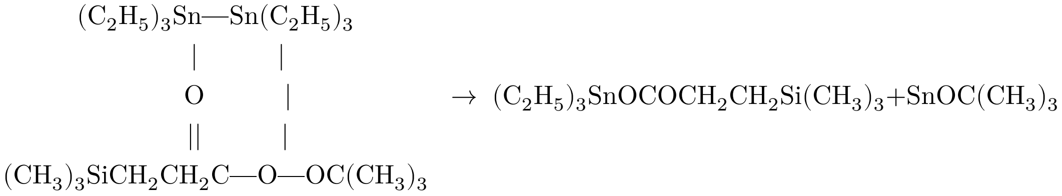
The nature of the other processes still remains unclear, since their other products are complex resinous compounds. We have shown that, upon decomposition of peresters in chlorobenzene, ethylene, hexamethyldisilane, or trimethylchlorosilane are not formed. This can be explained by the stability of $(CH_3)_3SiCH_2CH_2\cdot$ radicals toward decomposition into ethylene and $(CH_3)_3Si\cdot$ radicals. The absence (or very low yield) of 1,4-bis(trimethylsilyl)butane and trimethylvinylsilane shows that $(CH_3)_3SiCH_2CH_2\cdot$ radicals are reactive and are not inclined toward disproportionation or dimerization. It is interesting to note that $(C_2H_5)_3SiCH{-}CH_3$ radicals obtained by the action of peroxide on tetraethylsilane (^{7}, ^{8}) give the dimer in high yield. The reaction of tert-butyl β-(trimethylsilyl)perpropionate with tetraethyltin proceeds with homolysis of the Sn–C bond and formation of ethane, ethylene, β-(trimethylsilyl)propionic acid, and its $(C_2H_5)_3Sn$ salt. The yield of ethylene is high in comparison with the yield of ethane. The yield of CO_2, and especially of methane, is low (Table 1, experiment 3). The latter fact can be explained by assuming that reactions (2) and (3) are suppressed by the competing processes (5) and (6)

$$\begin{array}{c} \mathrm{R}\cdot + (C_2H_5)_4Sn \rightarrow RH + (C_2H_5)_3\dot{S}nC_2H_4 \\ \downarrow \\ (C_2H_5)_3Sn\cdot + C_2H_4, \end{array} \tag{5}$$

where $R = (CH_3)_3CO,\ (CH_3)_3SiCH_2CH_2CO_2,\ (CH_3)_3SiCH_2CH_2$

$$(CH_3)_3SiCH_2CH_2CO_2\cdot + (C_2H_5)_4Sn \rightarrow (C_2H_5)_3SnOCOCH_2CH_2Si(CH_3)_3 + C_2H_5\cdot \tag{6}$$

Another explanation is also admissible: in the medium of tetraethyltin, the free-radical reactions (1)–(3) are accompanied by concealed-radical processes, not giving kinetically independent $(CH_3)_3SiCH_2CH_2CO_2\cdot$ and $(CH_3)_3CO\cdot$ radicals. The possibility of such processes was substantiated by us earlier ([7,8]). Other features of the reactions of tetraethyltin with organic peroxides are discussed there as well. The perester reacts with hexaethyldistannane in an entirely different way (Table 1, experiment 4). The reaction is complete in 2 hours at 100°. Under these conditions the starting reagents separately are sufficiently stable. Its main products are triethyltin β-(trimethylsilyl)propionate and triethyl(tert-butoxy)tin. Traces of tert-butanol, acetone, and methane are formed as by-products. It may be assumed that the reaction proceeds with intermediate formation of a complex, which subsequently decomposes with homolysis of the O—O and Sn—Sn bonds.



$$\begin{array}{lcl} & (C_2H_5)_3Sn & \text{—}Sn(C_2H_5)_3 \\ & | & \quad | \\ & O & \quad | \\ & \| & \quad | \\ (CH_3)_3SiCH_2CH_2 & C & \text{—}O\text{—}OC(CH_3)_3 \end{array} \rightarrow (C_2H_5)_3SnOCOCH_2CH_2Si(CH_3)_3 + SnOC(CH_3)_3$$

Experimental Part

tert-Butyl ester of β-(trimethylsilyl)perpropionic acid. A solution of 8.2 g of β-(trimethylsilyl)propionic acid chloride in 30 ml of ether is added dropwise at 40° (bath temperature) to a stirred mixture of 11.2 g of the sodium salt of tert-butyl hydroperoxide (peroxide content in the salt $\sim$ 51%) and 20 ml of ether. The mixture is stirred for another 5 h at the same temperature, 2.5 ml of 2 N NaOH solution is added, and the mixture is stirred again for 0.5 h. The ether layer is separated, washed with water, dried over $MgSO_4$, and fractionated. This gives 6.5 g (60%) of the tert-butyl ester of β-(trimethylsilyl)perpropionic acid. B.p. 59–60° at 0.5 mm, n_D^{20} 1.4312, d_4^{20} 1.9085; MR_D found 59.23, calculated 61.32. Mol. wt.: found 208.2 (benzene), calculated 218.4.

Found, %:	C 54.40; H 10.22; O_{act} 7.18
$C_{10}H_{22}O_3Si$. Calculated, %:	C 55.01; H 10.15; O_{act} 7.33

The active oxygen is determined iodometrically by an analogous procedure ([9]).

The reactions of decomposition of the perester are studied in the apparatus described earlier ([8]). The results are summarized in Table 1. A typical experiment is given below.

Decomposition of the perester in chlorobenzene. A solution of 2.79 g of the perester in 101.2 g of chlorobenzene is thermostatted for 7 h at 126° under nitrogen. The yield of CO_2 is determined from the gain in weight of the absorbers; methane is identified chromatographically. The volatile products are separated from the reaction mixture by vacuum recondensation. From these, tert-butanol, b.p. 82°, n_D^{20} 1.3880, is isolated by fractionation. Acetone is identified as the 2,4-dinitrophenylhydrazone, m.p. 126°. In a parallel experiment, the yields of acetone (by oximation according to (^{10})) and tert-butanol (by the method of Tserevitinov) are determined.

By a spectrophotometric method, trimethylethylsilane is identified in the volatile fraction (absorption bands at 1243 and 840 cm^{-1}, which agrees with data (^{11})). The high-boiling residue is dissolved in ether and extracted with sodium carbonate solution. From the sodium carbonate extracts, β-(trimethylsilyl)propionic acid is isolated in the usual way. B.p. 113–117° at 20 mm; n_D^{20} 1.4260. According to data (^{11}): b.p. 114–116° at 20 mm; n_D^{20} 1.4257. The ether solution is washed with water, dried over $CaCl_2$, and distilled. A substance is isolated with b.p. 99–102° at 9 mm; n_D^{20} 1.4945; d_4^{20} 0.9512.

Its IR spectrum has absorption bands which, according to the data of (11), correspond to the presence of a benzene ring (1590 and 1480 cm^{-1}), a chlorine bond with the benzene ring (820 cm^{-1}), an Si–CH_2 bond (1245 cm^{-1}), and a $(CH_3)_3Si$ group (1250, 840, and 755 cm^{-1}). This makes it possible to assign to the substance the structure of β-(chlorophenyl)ethyltrimethylsilane.

Found, %: Cl 15.90; Si 13.60
$C_{11}H_{17}ClSi$. Calculated, %: Cl 16.66; Si 13.19

In addition, 1.6 g of a resin containing 15.1% chlorine and ( )8.5% silicon is isolated from the ether solution.

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Received
19 II 1965

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