EFFECT OF SOLVENT ON THE MECHANISM OF THE THERMAL DECOMPOSITION OF THE CUMENYL ESTER OF β-(TRIMETHYLSILYL)PERPROPIONIC ACID

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We have previously shown that in the absence of solvent the cumenyl ester of β-(trimethylsilyl)perpropionic acid undergoes heterolytic rearrangement [1] but is homolytically cleaved in cumene [2]. In this study we have carried out a more detailed investigation of the effect of the nature of the solvent on the mechanism for decomposition of the perester. In n-nonane (Table 1, experiment 1) at 120-125° the decomposition proceeds via a homolytic scheme with the intermediate formation of $(CH_3)_3SiCH_2CH_2COO^{\bullet}$ and $C_6H_5(CH_3)_2CO^{\bullet}$ radicals. The latter are stabilized due to removal of hydrogen from the solvent, which leads to the formation of β-(trimethylsilyl)propionic acid and cumenyl alcohol. In addition, judging from the presence of CO_2 and acetophenone in the reaction mixture, these radicals can undergo decomposition via the equation

$$(CH_3)_3SiCH_2CH_2COO^{\bullet} \rightarrow CO_2 + (CH_3)_3SiCH_2CH_2^{\bullet},$$
$$C_6H_5\,(CH_3)_2CO^{\bullet} \rightarrow C_6H_5COCH_3 + CH_3^{\bullet}.$$

The secondary $(CH_3)_3SiCH_2CH_2^{\bullet}$ radicals formed disproportionate to form ethyltrimethyl- and vinyltrimethylsilane, while the methyl group is converted to methane by removing a hydrogen from the surrounding molecules.

If an equimolar amount of trifluoroacetic acid is added to the perester dissolved in nonane, a sharp change in the decomposition mechanism is observed (see Table 1). In this case, the reaction proceeds under considerably milder conditions (20°), and its major products are phenol, acetone, β-(trimethylsilyl)propionic acid, and α-methylvinyl phenyl ether, which attests to heterolytic rearrangement of the starting perester. Trifluoroacetic acid probably favors polarization of the O–O bond in the perester [3-6], as a result of which its rearrangement, which involves migration of the phenyl ring from the carbon atom to the oxygen atom, becomes possible:

$$(CH_3)_3SiCH_2CH_2C\,(O)OOC\,(CH_3)_2C_6H_5 \rightarrow [(CH_3)_3SiCH_2CH_2C(O)OC(OC_6H_5)\cdot$$
$$\cdot(CH_3)_2]\ (A)$$

Intermediate (A) partially decomposes to the acid and α-methylvinyl phenyl ether and is partially hydrolyzed by the water introduced with the trifluoroacetic acid:

$$(A) - \left[\begin{array}{l} \longrightarrow (CH_3)_3SiCH_2CH_2COOH + C_6H_5OC\,(CH_3){=}CH_2 \\ \\ \xrightarrow{H_2O} (CH_3)_3SiCH_2CH_2COOH + C_6H_5OH + CH_3COCH_3 \end{array}\right.$$

Heterolytic rearrangement occurs during the decomposition of the perester in absolute methanol (experiment 3). However, in this system the decomposition of intermediate (A) is markedly suppressed by methanolysis of this compound:

$$(A) + CH_3OH \rightarrow (CH_3)_3SiCH_2CH_2COOCH_3 + C_6H_5OH + CH_3COCH_3.$$

We could not detect products of the free-radical decomposition of the perester in reactions carried out with added trifluoroacetic acid or in methanol. However, if nitrobenzene is used as the solvent (experiment 4), the heterolytic rearrangement process, which leads to the formation of α-methylvinyl phenyl ether,

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TABLE 1

Expt. No.	Materials used in the reaction, mole	T, °C	Time, h	Reaction products, mole per mole of peroxide
1	0,01 (I) 0,20 $n\text{-}C_9H_{20}$	120—125	4	0,78 CO_2; 0,17 $(CH_3)_3SiCH_2CH_2COOH$ 0,54 $C_6H_5(CH_3)_2COH$; 0,46 $C_6H_5COCH_3$ 0,50 CH_4; 0,36 $(CH_3)_3SiC_2H_5$ 0,35 $(CH_3)_3SiCH=CH_2$
2	0,01 (I) 0,01 CF_3COOH 0,20 $n\text{-}C_9H_{20}$	20	3	0,96 $(CH_3)_3SiCHCH_2COOH$ 0,60 C_6H_5OH; 0,21 $C_6H_5OC(CH_3)=CH_2$ 0,58 $(CH_3)_2CO$
3	0,01 (I) 0,80 CH_3OH	50—60	20	0,97 C_6H_5OH; 0,72 $(CH_3)_3SiCH_2CH_2C(O)OCH_3$ 0,62 $(CH_3)_2CO$; 0,14 $(CH_3)_3SiCH_2CH_2COOH$ 0,05 $C_6H_5OC(CH_3)=CH_2$
4	0,01 (I) 0,20 $C_6H_5NO_2$	90	4	0,45 CO_2; 0,51 $(CH_3)_3SiCH_2CH_2COOH$ 0,23 $C_6H_5(CH_3)_2COH$; 0,40 $C_6H_5COCH_3$ 0,45 CH_4; 0,18 $C_6H_5OC(CH_3)=CH_2$ 0,03 $[(CH_3)_3SiCH_2CH_2]_2$ 0,18 $(CH_3)_3SiC_2H_5$; 0,17 $(CH_3)_3SiCH=CH_2$
5	0,01 (I) 0,20 $(C_2H_5)_4Sn$	120—125	4	0,30 CO_2; 0,58 $(C_2H_5)_3SnOCOCH_2CH_2Si(CH_3)_3$ 1,00 $C_6H_5(CH_3)_2COH$; 0,18 $(CH_3)_3SiC_2H_5$ 0,19 $(CH_3)_3SiCH=CH_2$; 0,46 C_2H_6; 0,41 C_2H_4

is suppressed to a considerable degree by homolytic decomposition of the perester. This can be judged from the rather high yield of CO_2, methane, and other products.

Finally, we studied the decomposition of the perester in tetraethylstannane (experiment 5). As in n-nonane, in this medium the decomposition proceeds at an appreciable rate at 120-125°. In addition, the reaction is characterized by a low yield of CO_2, a quantitative yield of cumenyl alcohol, and by the absence of free $(CH_3)_3SiCH_2CH_2COOH$ in the reaction mixture. Moreover, one observes the formation of triethyl[β-(trimethylsilyl)propionyloxy]stannane, which cannot be explained by acidolysis:

$$(CH_3)_3SiCH_2CH_2COOH + (C_2H_5)_4Sn \rightarrow (C_2H_5)_3SnOCOCH_2CH_2Si(CH_3)_3 + C_2H_6,$$

since, in addition to ethane, the mixture contains an equimolar amount of ethylene. It is more likely that these gaseous products are formed by disproportionation of $C_2H_5^{\bullet}$ radicals.

All of these peculiarities can be explained either by crypto-radical interaction of the perester with tetraethylstannane [7] or by the distinctly expressed induced decomposition of the peroxide by $(C_2H_5)_3Sn^{\bullet}$ radicals [8]. In both cases the probability of the formation of $(CH_3)_3SiCH_2CH_2COO^{\bullet}$ free radicals and, consequently, their conversion products should decrease.

EXPERIMENTAL METHOD

Decomposition of the Cumenyl Ester of β-(Trimethylsilyl)perpropionic Acid (I) in Nitrobenzene. A solution of 2.8 g of (I) in 25 g of nitrobenzene was heated for 4 h at 90° under argon. The yield of CO_2 was determined from the increase in weight of absorbers filled with 30% KOH. The highly volatile products [$(CH_3)_3SiC_2H_5$ and $(CH_3)_3SiC_2H_3$] were separated by recondensation in vacuo and analyzed by gas–liquid chromatography ("Tswett-4" chromatograph, 15% PEG-20M on Chromosorb-W, 58°, helium gas carrier). The yield of $(CH_3)_3SiCH_2CH_2COOH$ was determined in an aliquot of the high-boiling residue by titration. To isolate the acid, the residue (from several experiments) was extracted with Na_2CO_3 solution. The sodium carbonate extracts yielded an acid with bp 113-117° (20 mm); n_D^{20} 1.4257 [9]. The cumenyl alcohol, acetophenone, α-methylvinyl phenyl ether, and 1,4-bis(trimethylsilyl)butane in the neutral portion of the high-boiling residue were identified and their yields determined by gas–liquid chromatography ("Tswett-1" chromatograph, 7% PEG on INZ-600, 180°, helium gas carrier) (see Table 1, experiment 4).

The reaction mixtures obtained from the decomposition of (I) in n-nonane and tetraethylstannane were similarly analyzed.

Decomposition of (I) in Absolute Methanol. A solution of 2.8 g of (I) in 26 g of methanol was heated in a sealed, evacuated ampul at 50-60° for 20 h. The ampul was connected to CO_2 absorbers and opened. No change was observed in the weight of the absorbers. The acetone in the highly volatile fraction was determined as the 2,4-dinitrophenylhydrazone with mp 123°. The $(CH_3)_3SiCH_2CH_2COOH$ (see above) was isolated from the high-boiling residue by the usual method. The neutral portion of the residue was analyzed by gas –liquid chromatography ("Tswett-3" chromatograph, 15% PEG-20 on Aerosil, 140°, helium gas carrier).

To identify the $(CH_3)_3SiCH_2CH_2COOCH_3$, this ester was obtained by alternative synthesis by heating a mixture of 2.9 g $(CH_3)_3SiCH_2CH_2COOH$, 20 g of methanol, and 0.2 ml of H_2SO_4 in 6 ml of CCl_4 to the boiling point for 10 h. The usual workup of the mixture yielded 1.0 g (30%) of ester with bp 63-64° (26 mm); n_D^{20} 1.4205. Found: C 52.71; H 10.30; Si 16.84%. $C_7H_{16}SiO_2$. Calculated: C 52.45; H 10.06; Si 17.52%.

CONCLUSIONS

The thermal decomposition of the cumenyl ester of β-(trimethylsilyl)perpropionic acid in n-nonane and tetraethylstannane proceeds via a homolytic mechanism; heterolytic rearrangement of the perester with subsequent solvolysis and (or) decomposition of the rearranged product occurs in polar solvents (nitrobenzene and methanol) or in n-nonane containing trifluoroacetic acid.

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