gave 8.2 g (74%) of DPU. The solvent was removed from the ether solution in vacuo and the residue was distilled to give 3.8 g of (VI), bp 127-129° (0.2 mm), n_D^{20} 1.4270. Found: C 32.93; H 6.45; P 20.76%. $C_8H_{20}O_7P_2$. Calculated: C 33.10; H 6.85; P 21.40%. δ ^{31}P; −15 ppm. (cf. [9]).

CONCLUSIONS

1. The reaction of diphenylurea with the chlorides of phosphorous and phosphonous esters gives phosphorylated urea derivatives, whereas reaction with the chloride of diethylphosphoric acid leads to tetraethyl pyrophosphate and diphenylcarbodiimide.

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THERMAL DECOMPOSITION OF TRIMETHYLSILYL tert-BUTYL PERSUCCINATE

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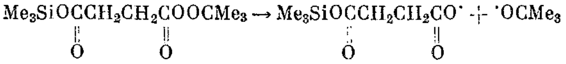
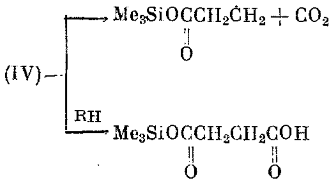
As a continuation of studying the reactivity of silicon-containing radicals, formed during the thermal decomposition of trimethylsilyl tert-butyl perphthalate (I) and trimethylsilyl tert-butyl permaleate (II), we made a study of the thermal decomposition of trimethylsilyl tert-butyl persuccinate (III) without a solvent and in either benzene or cumene. The purpose of the study was to ascertain the effect of varying the hydrocarbon fragment in the acyl portion of the peroxide on the behavior of the formed radicals. The complete decomposition of (III) proceeds at 110-115°C in 25 h. On the basis of the kinetic studies and the thermal decomposition products (Table 1) it may be concluded that the initial reaction act is homolysis of the peroxyester at the O—O bond.



$$\mathrm{Me_3SiO\underset{\underset{O}{\|}}{C}CH_2CH_2\underset{\underset{O}{\|}}{C}OOCMe_3 \rightarrow Me_3SiO\underset{\underset{O}{\|}}{C}CH_2CH_2\underset{\underset{O}{\|}}{C}O^{\cdot} + {}^{\cdot}OCMe_3}$$

(III) (IV)

The formed Si-containing acyloxy radicals (IV) are unstable and mainly undergo fragmentation with the elimination of CO_2, whose yield reaches 79-88%. Only a small part of (IV) cleaves hydrogen and is converted to the acid trimethylsilyl succinate.



$$\text{(IV)} \rightarrow \begin{cases} \mathrm{Me_3SiO\underset{\underset{O}{\|}}{C}CH_2\dot{C}H_2 + CO_2} \\ \xrightarrow{\mathrm{RH}} \mathrm{Me_3SiO\underset{\underset{O}{\|}}{C}CH_2CH_2\underset{\underset{O}{\|}}{C}OH} \end{cases}$$

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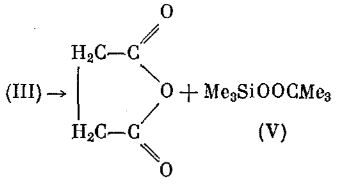
TABLE 1. Thermolysis Products of Trimethylsilyl tert-Butyl Persuccinate (110-115°)

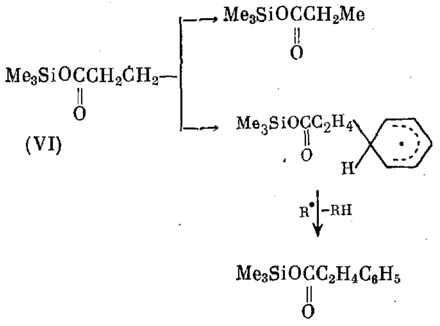
Product	Yield, mole/mole of perester		
	no solvent	in benzene	in cumene
CO_2	0,88	0,85	0,79
CH_4	0,43	0,38	0,10
MeCOMe	0,42	0,44	0,08
Me_3COH	0,29	0,32	0,69
$Me_3SiOSiMe_3$	0,05	0,03	0,02
$Me_3SiOOCMe_3$	0,02	0,01	–
$Me_3SiOC(O)CH_2Me$	0,21	0,16	0,55
$Me_3SiOC(O)C_2H_4C_6H_5$	–	0,26	–
Dicumyl	–	–	0,66
After hydrolysis and methylation of high-boiling residue			
$Me_3SiOSiMe_3$	0,29	0,20	0,16
$MeOC(O)C_2H_4OCMe_3$	0,32	0,16	0,20
$MeOC(O)C_2H_4C(O)OMe$	0,08	0,07	0,09
$MeOC(O)C_2H_4C(O)OCH_2Me$	0,02	–	–
Unidentified product, %	18	16	7

Cyclization of the acyloxy radicals to succinic anhydride, which is observed for the carbon analog of (IV) [1], does not occur in the given case. Succinic anhydride, found in an amount of 2% in the reaction products, judging by the yield of trimethylsilyl tert-butyl peroxide (V), is formed by the following reaction:



In contrast to (III), the corresponding anhydrides (phthalic and maleic) are formed from (I) and (II) under analogous conditions in 20-30% yield [2, 3], which can be explained by the different geometry of their molecules. Peroxyesters (I) and (II) have rigid structures with a cis arrangement of the peroxyester and Si-containing groupings, whereas in (III) they can rotate freely around the C—C bond and occupy a greater distance between each other.

As was mentioned above, the decomposition of (III) proceeds with a high yield of CO_2, and consequently of carbotrimethylsiloxyethyl radicals (VI). The latter easily cleave hydrogen and substitute benzene by the homolytic mechanism to give respectively trimethylsilyl propionate and the trimethylsilyl ester of hydrocinnamic acid. The structurally analogous radicals $CH_3OC(O)CH_2CH_2\dot{C}H_2$ [4] and $(CH_3CH_2)_3GeOC(O)CH_2\dot{C}H_2$ [5] behave in a similar manner. The yield of the substitution product by Si-containing radicals is close to that of the Ge analog and nearly twice the yield of the carbon analog.



When (III) decomposes in cumene, the processes that relate to the cleavage of hydrogen from the solvent predominante, as is evidenced by the high yields of trimethylsilyl propionate (55%) and tert-butanol (69%). Homolytic substitution in the ring is practically nil. In addition, the trimethylsilyl ester of β-tert-butoxypropionic acid, which was identified as the methyl ester of this acid, is formed as the result of intracage recombination.

$$\left[\mathrm{Me_3Si\overset{}{O}\underset{\|\atop O}{C}CH_2CH_2\cdot\cdot\underset{\|\atop O}{C}O\cdot\cdot OCMe_3}\right]\rightarrow \mathrm{Me_3SiO\underset{\|\atop O}{C}CH_2CH_2OCMe_3} + CO_2$$

TABLE 2. Kinetic Parameters of Thermal Decomposition of Peroxides

Peroxide	$K_d \cdot 10^5$, sec^{-1} at t, °C				E_a, kcal/mole
	105	110	115	120	
$Me_3SiOC(O)C_2H_4C(O)OOCMe_3$	1,1	2,1	3,7	7,6	36,5
$Me\ OC(O)C_2H_4C(O)OOCMe_3$ *	–	2,4	4,2	7,8	37,6
$EtOC(O)C_2H_4C(O)OOCMe_3$ *	–	2,9	6,0	10,2	37,5

*Data from [6].

The process for the thermal decomposition of (III) in cumene at 105–120° is described by a first-order equation in peroxide. The initial concentration of the peroxyester has no effect on the reaction rate constant, which testifies that the induced decomposition of (III) is absent. The decomposition rate of peroxyester (III) is close to that of its carbon analogs: methoxy tert-butylperoxy (VII) and ethoxy tert-butylperoxy (VIII) succinate [6] (Table 2).

As a result, replacing either methyl or ethyl by the trimethylsilyl group has practically no effect on the thermal stability of perester (III).

EXPERIMENTAL

Trimethylsilyl tert-butyl persuccinate (III) was obtained as described in [2].

Decomposition of Perester (III) without a Solvent. Perester (III) was heated for 25 h at 110–115° in a sealed evacuated ampul equipped with an outlet. The volatile products were frozen in the outlet. The composition of the products was determined by GLC in a helium stream using a Tswett-102 chromatograph equipped with a katharometer: a) the gaseous products at 65° using a 2 m × 3 mm column packed with Silica Gel-3; b) $Me_3SiOSiMe_3$, $Me_3SiOCMe_3$ (V), t-BuOH, and acetone at 70° using a 3 m × 3 mm column packed with 15% Rheoplex deposited on Chromaton; c) $Me_3SiOC(O)CH_2CH_3$ at 80° using a 3 m × 3 mm column packed with 15% Apiezon deposited on Chromosorb W. The high-boiling decomposition products were determined via the products of their hydrolysis and methylation with an ether solution of diazomethane. The amounts of methyl ethyl succinate (from succinic anhydride) and dimethyl succinate (from succinic acid) were determined by GLC (140°, 3 m × 3 mm column packed with 15% Rheoplex deposited on Chromaton). The compounds were identified by comparing the retention times of the reaction products with those of known compounds. From the methylation products we also isolated the methyl ester of β-tert-butoxypropionic acid, n_D^{20} 1.4275. Found: C 59.72; H 9.56%. $C_8H_{16}O_2$. Calculated: C 60.00; H 10.00%. The IR and PMR spectra confirm the structure of the given compound.

Decomposition of Perester (III) in Benzene or Cumene. The decomposition of (III) was run in sealed evacuated ampuls at 110–115° for 25 h. The composition of the reaction products was determined the same as above. When the thermolysis of (III) was run in benzene, the Si ester of hydrocinnamic acid was determined by GLC (175°, 1 m × 3 mm column packed with 5% SE-30 deposited on Inerton).

The kinetic measurements of the thermal decomposition of (III) were run in cumene in a thermostatted apparatus, through which a steady stream of dry argon was passed. The temperature was maintained constant with an accuracy of ± 1°. The initial concentration of the peroxide was 0.02 mole/liter. The decomposition rate was checked iodometrically by the change in the concentration of peroxide oxygen.

CONCLUSIONS

1. The decomposition of trimethylsilyl tert-butyl persuccinate in the absence of a solvent, and also in benzene or cumene, begins with cleavage of the O–O bond.

2. The formed Si-containing acyloxy radicals mainly undergo fragmentation with the elimination of CO_2, and are converted to carbotrimethylsiloxyethyl radicals. The latter either cleave hydrogen from the solvent (cumene) or alkylate benzene by the homolytic substitution mechanism. The recombination of the radicals in the solvent cage is 16–20%.

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REACTION OF HYPOPHOSPHOROUS ACID WITH BENZALDEHYDE

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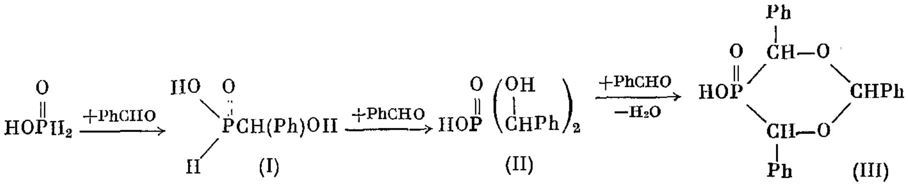
The formation of α-hydroxybenzylphosphonous acid (I), bis(α-hydroxybenzyl)phosphinic acid (II), and 5-hydroxy-5-oxo-2,4,6-triphenyl-1,3,5-dioxophosphorinane (III) is possible when hypophosphorous acid (HPA) reacts with benzaldehyde. However, a comparison of the constants and conditions for the formation of these products [1-5] leads to the conclusion that contradictions exist. Thus, in [1], using a 1: 2 ratio of HPA to benzaldehyde, a product with mp 165°C was isolated, which was assigned the structure of (II). In [2], using a 1: 1 ratio of the reactants, a product was obtained that was identified as being (I). But in [3], using the same ratio of the reactants, only a product with mp 230° was isolated, which was described as being (II), while the monoproduct was obtained using a threefold excess of HPA. In contrast, in [4], like in [1], the product, characterized as being (II), is formed with a 1: 3 ratio of HPA to benzaldehyde, but with mp 203-204°.

In [1-3] the structure of the products was established on the basis of the preparation method, elemental analysis, and the chemical properties. The PMR spectra were discussed in [4]. In the present paper the reaction of HPA with benzaldehyde using various ratios of the reactants was studied by the ^{31}P NMR spectroscopy method.



The reaction of HPA with benzaldehyde using a 1: 1 ratio was run as described in [3]. When the reaction mixture was refluxed for 2 h a product with mp 182° was obtained in 50% yield (relative to HPA), whose IR spectrum had an absorption band at 3320 cm^{-1} and whose structure, based on the elementary analysis data, corresponded to (II). The signal of the P atom in the $^{31}P-\{^1H\}$ NMR spectrum of (II) lies at 41 ppm. It should be mentioned that the melting point of our obtained (II) differs from all of the previously given values.

The product with mp 182° was also isolated when 2 moles of benzaldehyde was reacted with 1 mole of HPA in benzene under the conditions of removing the water by azeotropic distillation. A lower yield of (II) can be explained by the milder reaction conditions. Other products were not detected.

Different results were obtained when we studied the reaction of HPA with 3 moles of benzaldehyde in benzene with removal of the water. Here (II) and a product with mp 203° were isolated in approximately equal ratios. The latter product lacked absorption in the 3100-3600 cm^{-1} region and, based on the elemental analysis data, corresponded to structure (III). The chemical shift (CS) of the signal of the P atom in the $^{31}P-\{^1H\}$

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