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Abstract

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Rearrangement of Certain Organo-tin and Organo-lead Peroxide Compounds

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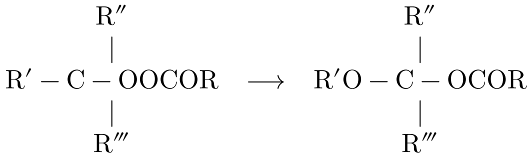
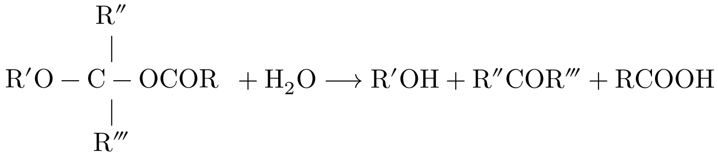
Recently there has been great interest in the investigation of organometallic peroxide compounds. In a recently published review (1), the methods of synthesis and the reactions of organometallic peroxide compounds known at present are discussed in detail. It could be assumed that some organometallic peroxide compounds are capable of undergoing rearrangements analogous to perester rearrangements. As is known, Wieland and Meyer observed the perester rearrangement of triphenylmethyl perbenzoate as early as thirty years ago (2). Considerably later, using decalin perbenzoate as an example (3), a rearrangement of this type was studied, and some regularities in the course of such processes were established. Following this work, a number of other authors (4–8) published their studies aimed at elucidating the mechanism of rearrangement of various peresters. It was established that the mechanism of perester rearrangement is reduced to migration of an alkyl or aryl group from the carbon atom bonded to the peroxide group to the oxygen atom of this group



$$R'-\overset{\displaystyle R''}{\underset{\displaystyle R'''}{\overset{|}{\underset{|}{C}}}}-OOCOR \longrightarrow R'O-\overset{\displaystyle R''}{\underset{\displaystyle R'''}{\overset{|}{\underset{|}{C}}}}-OCOR \qquad (1)$$

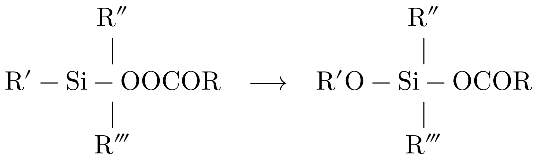
After hydrolysis of the rearrangement product, an alcohol, a carbonyl compound, and an acid are obtained



$$R'O-\overset{\displaystyle R''}{\underset{\displaystyle R'''}{\overset{|}{\underset{|}{C}}}}-OCOR + H_2O \longrightarrow R'OH + R''COR''' + RCOOH \qquad (2)$$

Several years ago, a rearrangement of this type was observed for peroxide compounds of silicon, which in chemical properties is the closest analog of carbon. It was found that, when an attempt was made to obtain trimethylsilyl perbenzoate from trimethylchlorosilane and perbenzoic acid in the presence of ammonia, a product containing no peroxide oxygen was formed, which readily underwent hydrolysis with liberation of benzoic acid. In the case of the analogous reaction of dimethylphenylchlorosilane, upon hydrolysis of the compound formed, phenol was isolated, the yield of which was 66% of the theoretically calculated amount (9). Phenol was also found in the reaction products of dimethylphenylchlorosilane with hydrogen peroxide in glacial acetic acid in the presence of small amounts of conc. H_2SO_4.

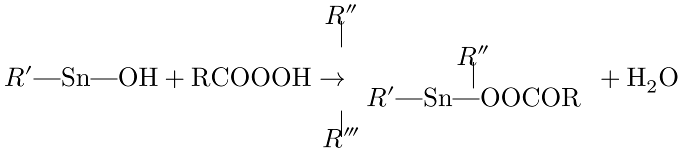
In both of these reactions one may assume the formation of the corresponding organosilicon peroxide compounds, which, like peresters, underwent heterolytic rearrangement



$$R' - \underset{\displaystyle R'''}{\overset{\displaystyle R''}{\mathrm{Si}}} - \mathrm{OOCOR} \longrightarrow R'\mathrm{O} - \underset{\displaystyle R'''}{\overset{\displaystyle R''}{\mathrm{Si}}} - \mathrm{OCOR} \qquad (3)$$

Hydrolysis of the product of reaction (3) was accompanied by the formation of the compounds indicated above. There are indications [10] of the occurrence of a rearrangement, analogous to the rearrangement of peresters, for the corresponding peroxide compounds of germanium. We have studied the analogous rearrangement of organotin and organolead peroxide compounds.

As is known, monohydroxy trialkyl- or triaryltin and -lead compounds possess strongly pronounced basic properties. Consequently, such compounds should react exceptionally readily with peracids to form the corresponding organometallic peroxide compounds



$$R'\text{—}\mathrm{Sn}\text{—}\mathrm{OH} + \mathrm{RCOOOH} \underset{R'''}{\overset{R''}{\rightarrow}} R'\text{—}\overset{R''}{\mathrm{Sn}}\text{—}\mathrm{OOCOR} + H_2O \qquad (4)$$

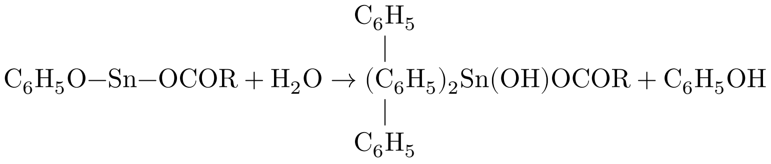
This organometallic peroxide compound can undergo rearrangement according to reaction (1). Hydrolysis of the rearrangement product formed in this process should be accompanied by the liberation of the corresponding oxide organometallic compounds, as well as other oxygen-containing compounds, which we did in fact observe. A homogeneous reaction mixture, obtained by mixing at 0°C solutions of equimolar amounts of triphenyltin monohydroxide and peracetic or perpropionic acid in thoroughly dried methanol (the initial concentration of the starting substances in the solution was 0.2 mole/liter), was left to stand in a dark place at room temperature for 40–50 hours. During this time the peroxide compounds in the solution were consumed completely, and well-formed needle-like crystals gradually separated from the solution. No gas evolution was observed in this reaction.

The precipitates separated from the solution and thoroughly washed with methyl alcohol were, in the case of peracetic acid, infusible up to 230°, and in the case of perpropionic acid, softened at 170° and on further heating formed nonfusible products; they were insoluble in cold benzene and only slightly soluble in hot benzene. Acid hydrolysis in both cases proved the liberation of free acetic or propionic acid. From the amount of organic acids liberated and from the formation of $(C_6H_5)_2Sn(OH)Cl$ (m.p. 185°, according to [11] 187°) upon heating the precipitates with hydrochloric acid, it may be concluded that, during rearrangement of the corresponding organotin peroxide compounds and their subsequent transformation, crystalline reaction products precipitated which were compounds of the type $(C_6H_5)_2Sn(OH)OCOR$ or $(C_6H_5)_2SnO \cdot (C_6H_5)_2Sn(OCOR)_2$. For alkyl derivatives of such organometallic compounds, corresponding indications are available in the literature [11].

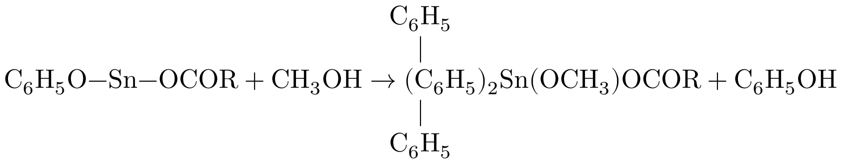
The yield of the reaction product $(C_6H_5)_2Sn(OH)OCOCH_3$ or $(C_6H_5)_2SnO \cdot (C_6H_5)_2Sn(OCOCH_3)_2$, calculated on the initial triphenyltin monohydroxide, was 72%. In the experiment with perpropionic acid, the yield of the corresponding compound that separated as a precipitate was 45%. However, upon alkaline hydrolysis of the compound remaining in the alcoholic solution, a considerable additional amount was obtained of a finely crystalline substance, insoluble in water but soluble in methanol and melting at 128–130°, which under the action of hydrochloric acid was converted into $(C_6H_5)_2Sn(OH)Cl$.

In the reaction with both peracetic and perpropionic acids, after separation of the solid transformation products and the unreacted triphenyltin monohydroxide, phenol was isolated from the reaction mixture and identified as tribromophenol (m.p. 95° from alcohol), melting without depression when mixed with an authentic sample. The yield of phenol in the reaction with both peracids was 90% of the theoretically calculated amount based on the initial hydroxide. The liberation of free phenol in the reacti-

of the mixture can be explained by the occurrence of the following reactions:



$$C_6H_5O{-}\overset{\displaystyle C_6H_5}{\underset{\displaystyle C_6H_5}{Sn}}{-}OCOR + H_2O \rightarrow (C_6H_5)_2Sn(OH)OCOR + C_6H_5OH \tag{5}$$



$$C_6H_5O{-}\overset{\displaystyle C_6H_5}{\underset{\displaystyle C_6H_5}{Sn}}{-}OCOR + CH_3OH \rightarrow (C_6H_5)_2Sn(OCH_3)OCOR + C_6H_5OH \tag{6}$$

In an analogous manner, we carried out the reaction of triphenyltin monohydroxide with peracetic acid in methyl alcohol, dioxane, and ether.

When the reaction was carried out in methyl alcohol, the homogeneous reaction mixture gave a negative test for peroxide oxygen after standing for 17 hours in a dark place at room temperature and subsequent heating at 50° for 2.5 hours. During this time there was a slight evolution of gas containing carbon dioxide, and a small amount of a precipitate of diphenyltin oxide fell out, identified as diphenyltin diacetate (m.p. 195—196°, m.p. of a mixed sample 198°). The precipitate was separated from the liquid reaction mixture by filtration. After treatment of the filtrate with aqueous alkali and separation of the white bulky precipitate that was thereby formed, phenol was isolated by the usual method; its yield was 38% calculated on the initial amount of triphenyltin monohydroxide. The above-mentioned water-insoluble precipitate was separated by boiling methanol into triphenyltin monohydroxide and diphenyltin oxide. In all, diphenyltin oxide was isolated from the reaction mixture in an amount of 35% of that calculated theoretically. The diphenyltin oxide was identified as diphenyltin diacetate, obtained by treating diphenyltin oxide with acetic acid in boiling methanol.

The reaction of triphenyltin monohydroxide with peracetic acid in dioxane proceeded slowly because of the comparatively poor solubility of the initial organolead compound. However, in this solvent also, after prolonged standing of the reaction mixture in a dark place at room temperature and subsequent heating for 3 hours at 50° and for one hour at 70°, phenol was isolated; its amount was 40% of that theoretically calculated for the triphenyltin monohydroxide taken. In this experiment, at the initial stage of the reaction, a brief but quite noticeable evolution of gas was observed and, moreover, the peroxide compound in the reaction mixture was not completely consumed during the entire period of observation.

When carrying out the reaction of peracetic acid with triphenyltin monohydroxide in sulfur ether, we encountered a difficulty caused by the negligibly small solubility of the initial organolead compound in this solvent. Nevertheless, in this case too, after shaking for two hours a heterogeneous mixture consisting of triphenyltin monohydroxide, peracetic acid, and sulfur ether, a compound passed into solution which, after hydrolysis, liberated phenol. The yield of the latter was about 3% of the amount calculated on the initial lead monohydroxide, which in the reaction was consumed only partially. In this experiment, as in the preceding one, a noticeable evolution of gas was observed at the very beginning of the reaction, but then it quickly ceased and subsequently did not occur at all.

Less definite results were obtained in studying the reaction of triethyltin monohydroxide with peracetic and perbenzoic acids. When an ethereal solution of peracetic acid cooled to −10° (initial concentration 0.33 mole/liter) was added to an equimolar amount of triethyltin monohydroxide at the same temperature, very poorly soluble in diethyl ether, went into solution very rapidly, which indicated a rapidly proceeding reaction between the starting substances with formation of a lead-organic peroxide compound. Rearrangement of this compound under the conditions of the experiment (temperature −10°) proceeded slowly, as indicated by the slow decrease in the concentration of peroxide oxygen in the ether solution. No gas evolution was observed, but large snow-white crystals separated, melting at 158° with decomposition. From the melting point of these crystals in the pure state and in a mixed sample with pure triethyllead acetate (m.p. 160°), the precipitate that separated was identified by us as triethyllead acetate. Its yield in a reaction mixture kept in the dark for 36 h at −10° was 75%, calculated on the initial triethyllead monohydroperoxide.

The reaction of triethyllead monohydroperoxide with peracetic acid in aqueous solution (initial concentration of the reactants 0.13 mol/l) at room temperature proceeded comparatively rapidly, with slight gas evolution. After the reaction mixture had stood in a dark place at room temperature for 24 h, no peroxide oxygen was detected in it, but acetaldehyde and tetraethyllead were detected qualitatively. The formation of acetaldehyde can be explained by mild oxidation by peracetic acid of the ethyl alcohol (12) liberated in a reaction analogous to reaction (5). Tetraethyllead may be the result of disproportionation of triethyllead acetate or diethyllead diacetate, which were formed in aqueous solution as a result of the main or side reactions (13).

The reaction of triethyllead monohydroperoxide with perbenzoic acid in diethyl ether proceeded analogously to the reaction with peracetic acid described above. When the reaction with perbenzoic acid was carried out first for one hour at −20 to −10°, and then for 12 h at room temperature, no peroxide oxygen was detected in the reaction mixture. From the solution there was then isolated triethyllead benzoate (m.p. 125–127°; the pure compound (14) has m.p. 127°) in an amount of 35%, calculated on the amount of triethyllead hydroxide taken for the reaction. Along with this compound there was formed a water-soluble lead-organic compound not further investigated by us. From its aqueous solution, on prolonged standing in air, a water-insoluble precipitate separated, which by its melting point (162°) was identified by us as diethyllead dibenzoate, having m.p. 168° (14).

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

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