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SYNTHESES OF DIETHYL(TRIPHENYLGERMYLPEROXY)THALLIUM AND DIETHYL(TRIPHENYLSILYLPEROXY)THALLIUM AND A STUDY OF THEIR REACTIVITIES

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SUMMARY

The reaction of triphenylgermyl hydroperoxide with triethylthallium gives a biorganometallic peroxide, diethyl(triphenylgermylperoxy)thallium, but the reaction of triphenylsilyl hydroperoxide with triethylthallium does not yield the corresponding pure biorganometallic peroxide as the latter undergoes a rearrangement. A similar rearrangement occurs if diethyl(triphenylgermylperoxy)thallium is heated at 80° when diethyl(diphenylphenoxygermyloxy)thallium is formed. It is shown that the rearrangement of this peroxide occurs via a second-order reaction whose activation energy is equal to 20.4 kcal·mol⁻¹.

Biorganometallic peroxides present an interesting field of research. Data exist regarding the synthesis and thermal decomposition of biorganometallic peroxides containing the M–O–O–M group, where M = metal; on heating symmetrical peroxide compounds containing tin[1] and germanium[2,3] to 80–120°, homolysis of the oxygen–oxygen bond occurs:

$$R_3MOOMR_3 \rightarrow 2\,R_3MO^{\bullet} \tag{1}$$

(M = Ge, Sn; R = Et, Ph)

Kinetic investigations of the reaction have shown that the process occurs by a first-order mechanism, whose activation energy is 33.7 kcal·mol⁻¹, and that with the germanium compound[2,3] rearrangement of the peroxide occurs according to the following radical scheme:

$$R_3GeO^{\bullet} \rightarrow R_2Ge^{\bullet}OR \tag{2}$$

$$R_3GeO^{\bullet} + R_2Ge^{\bullet}OR \rightarrow \underset{\text{(I)}}{R_3GeOGe(OR)R_2} \tag{3}$$

Product (I) was not obtained in a pure state.

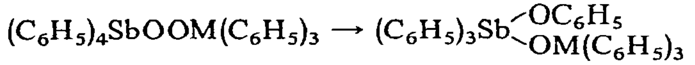
With the analogous silyl peroxides rearrangement occurs with the phenyl group migrating from the silicon atom to the oxygen atom[4].

$$(CH_3)_3SiOOSi(C_6H_5)_3 \rightarrow (CH_3)_3SiOSi(OC_6H_5)(C_6H_5)_2 \tag{4}$$

The rate of rearrangement increases as the dielectric constant of the medium increases, which is typical for a heterolytic reaction. The activation energy of the process is equal to 27.1–28.0 kcal · mol^{-1}.

Mixed biorganometallic peroxides containg Si and Ge, for example trimethyl(triphenylgermylperoxy)silane, triphenyl(triphenylgermylperoxy)silane and dimethylphenyl(triphenylgermylperoxy)silane, also undergo intramolecular rearrangement on being heated (100–120°) in various organic solvents with a corresponding migration of either the methyl or phenyl group from the silicon to the oxygen atom[5].

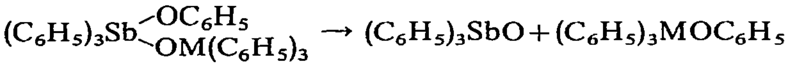
Bielementorganic peroxides of the type $(C_6H_5)_4SbOOM(C_6H_5)_3$ also rearrange under similar conditions[6]. With these peroxides the phenyl group migrates to the oxygen atom from the antimony atom:



$$(C_6H_5)_4SbOOM(C_6H_5)_3 \rightarrow (C_6H_5)_3Sb\begin{array}{l}\diagup OC_6H_5\\ \diagdown OM(C_6H_5)_3\end{array} \qquad (5)$$

(M = Si, Ge, Sn)

Under the conditions employed in the experiment (100°, 10 h) the rearranged product dissociates further to give triphenylantimony oxide and Group IV organometallic compounds:



$$(C_6H_5)_3Sb\begin{array}{l}\diagup OC_6H_5\\ \diagdown OM(C_6H_5)_3\end{array} \rightarrow (C_6H_5)_3SbO+(C_6H_5)_3MOC_6H_5 \qquad (6)$$

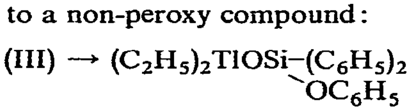
It is interesting to speculate whether a similar rearrangement would take place with organometallic peroxides containing a Group IV element and a Group III metal. Since the organometallic peroxides of thallium are relatively easily prepared by the reaction of equimolar quantities of triethylthallium with the corresponding organometallic hydroperoxides in benzene at 0° under argon[7], our studies have been confined to peroxides involving this metal.

$$(C_2H_5)_3Tl+(C_6H_5)_3MOOH \rightarrow (C_2H_5)_2TlOOM(C_6H_5)_3+C_2H_6 \qquad (7)$$

(II) M = Ge; (III) M = Si

The peroxide (II) proved to be a faintly yellow crystalline compound, labile at room temperature and sensitive to light, which liberates iodine from an acid solution of potassium iodide. Its IR spectrum contains an absorption band at 840 cm^{-1} which corresponds to the characteristic stretching mode for the oxygen–oxygen bond.

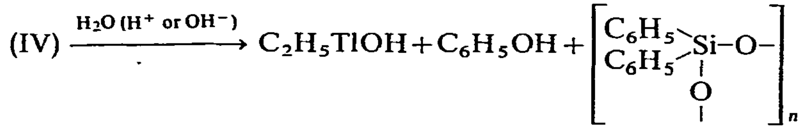
Reaction of triphenylsilyl hydroperoxide with triethylthallium did not result in the formation of the corresponding peroxide, despite the fact during the reaction approximately 1.0 mole of ethane was evolved in agreement with eqn. (7). It must be assumed that the initial peroxide (III) is so unstable that during its synthesis it rearranges to a non-peroxy compound:



$$(III) \rightarrow (C_2H_5)_2TlOSi\begin{array}{l}-(C_6H_5)_2\\ \diagdown OC_6H_5\end{array} \qquad (8)$$

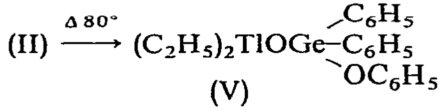
(IV)

The resulting diethyl(diphenylphenoxysilyloxy)thallium (IV) cannot be distilled even under vacuum, and is easily hydrolysed in the presence of acids as well as alkalis:



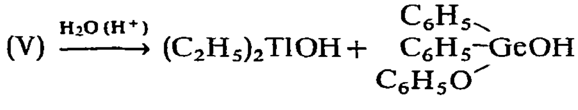
$$\text{(IV)} \xrightarrow{H_2O\,(H^+ \text{ or } OH^-)} C_2H_5TlOH + C_6H_5OH + \left[\begin{array}{c} \begin{array}{r} C_6H_5\diagdown \\ C_6H_5\diagup \end{array} Si{-}O{-} \\ | \\ O \\ | \end{array}\right]_n \qquad (9)$$

If the peroxide (II) is heated to 80° in a sealed, evacuated ampoule in the presence of cumene for 30–40 h it loses its peroxy oxygen. Diethyl(diphenylphenoxygermyloxy)thallium (V) is formed in quantitative yield, but dicumyl and oxygen were not found amoungst the reaction products. These results indicate that during heating the peroxide (II) undergoes the following rearrangement:



$$\text{(II)} \xrightarrow{\Delta\, 80^\circ} \underset{\text{(V)}}{(C_2H_5)_2TlOGe} \begin{array}{l} \diagup C_6H_5 \\ {-}C_6H_5 \\ \diagdown OC_6H_5 \end{array} \qquad (10)$$

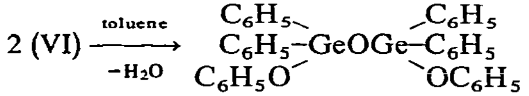
Hydrolysis of (V) gave diethylthallium hydroxide and diphenylphenoxygermanium hydroxide (VI):



$$\text{(V)} \xrightarrow{H_2O\,(H^+)} (C_2H_5)_2TlOH + \begin{array}{r} C_6H_5\diagdown \\ C_6H_5{-}GeOH \\ C_6H_5O\diagup \end{array} \qquad (11)$$

(VI)

Boiling (VI) in toluene solution for 4 h gave the corresponding oxide of germanium (VII):



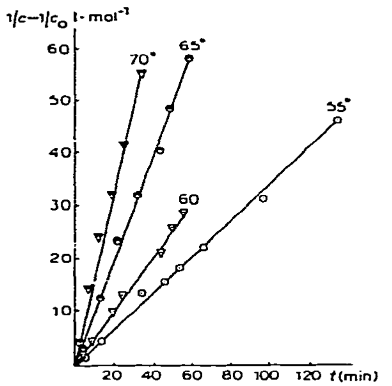
$$2\,\text{(VI)} \xrightarrow[-H_2O]{\text{toluene}} \begin{array}{r} C_6H_5\diagdown \\ C_6H_5{-}GeOGe \\ C_6H_5O\diagup \end{array} \begin{array}{l} \diagup C_6H_5 \\ {-}C_6H_5 \\ \diagdown OC_6H_5 \end{array} \qquad (12)$$

(VII)

In order to study the kinetic aspects of the rearrangement of peroxides, measurements of the reaction rate have been undertaken at five degree intervals over the temperature range 55–70°. Measurements were made iodimetrically on a benzene solution of the peroxide and the rates thus obtained are presented in Fig. 1. From this figure it will be seen that decomposition of peroxide (II) proceeds by a second-order mechanism, the rate increasing as the temperature increases. In order to confirm this observation, the thermal decomposition of the peroxide at various initial concentrations has been studied at 60° (Fig. 2). As the initial concentration of peroxide (II) increases the effective rate constant for the decomposition decreases in accordance with the behaviour expected for second-order reactions[8,9]. The product of the rearrangement, (V), has no influence whatsoever on the effective rate constant for the thermal decomposition of the peroxide (II). The semilogarithmic dependence between the effective rate constant for thermal peroxide decomposition and the temperature is in agreement with Arrhenius' equation and leads to an activation energy for the reaction of 20.4 kcal·mol^{-1}.

These results indicate that two molecules of the peroxide participate in the rearrangement, and that the reaction proceeds according to Scheme 1.

All peroxides which undergo this rearrangement possess a polar oxygen–oxygen bond. This is confirmed by the IR spectra of these compounds in which



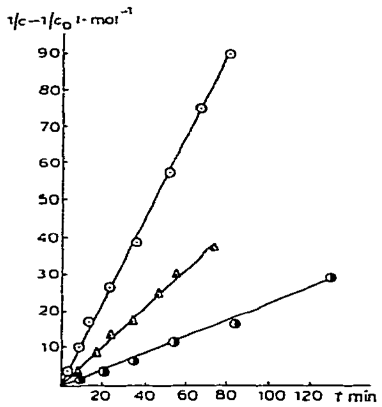
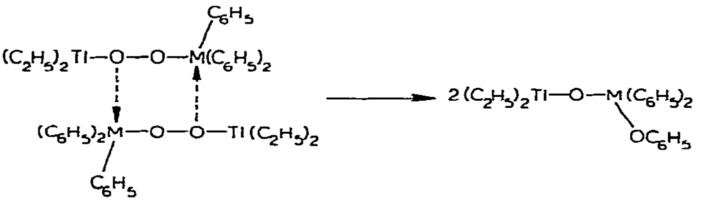


Fig. 1. Decomposition rates of $(C_2H_5)_2TlOOGe(C_6H_5)_3$ in benzene at various temperatures (initial peroxide concentration 0.020 M).

Fig. 2. Decomposition rates of $(C_2H_5)_2TlOOGe(C_6H_5)_3$ in benzene at 60° at various initial peroxide concentrations (c_0) (○ c_0 0.015 M: △ c_0 0.020 M: ◑ c_0 0.025 M).

SCHEME 1



stretching vibrations corresponding to the oxygen–oxygen linkage occur at the low frequency end of the spectrum. Thus, for bis(triphenylgermyl)peroxide and diethyl(triphenylgermylperoxy)thallium these vibrations appear, in both cases, at 848 cm^{-1}, in comparison with the stretching vibrations of oxygen–oxygen bonds of carbon peroxide compounds which occur at approximately 880 cm^{-1}.

EXPERIMENTAL

Synthesis of diethyl(triphenylgermylperoxy)thallium

This synthesis was carried out according to the procedure outlined in ref. 7. Triphenylgermyl hydroperoxide (2.43 g, 0.007 mole) was added to 65 ml benzene in a two-necked flask. The solution was degassed and the system filled with argon. Triethylthallium (2.10 g, 0.007 mole) and dry benzene (5 ml) contained in a special ampoule were also maintained under argon, and the ampoule connected to the reaction flask. Portions of the triethylthallium solution were added successively to the triphenylgermyl hydroperoxide solution while the ethane evolved (129 ml) was measured by means of a gas burette. The reaction mixture was maintained in complete darkness for 20–25 min. After this time the benzene solvent was evaporated, the precipitate formed recrystallized from pentane and analysed iodiometrically for its peroxide oxygen content. Yield 3.45 g (80%); purity 98.5%.

Diethyl(triphenylgermylperoxy)thallium is a pale yellow crystalline compound whose IR spectrum exhibits an absorption band at 840 cm^{-1}, corresponding to the oxygen–oxygen vibration for organometallic peroxides.

Reaction of triphenylsilyl hydroperoxide with triethylthallium

This reaction was carried out in the same way as the synthesis of diethyl(triphenylgermylperoxy)thallium. A solution of triethylthallium (1.23 g, 0.042 mole) in 5 ml of benzene was added to a solution of triphenylsilyl hydroperoxide (1.25 g, 0.042 mole) in 10 ml of benzene. When an exothermic reaction occurred 68.5 ml of ethane was generated. The reaction mixture was kept in total darkness at room temperature for 30–40 min, the solvent was then evaporated, and diethyl(diphenylphenoxysilyloxy)thallium (1.62 g, 0.028 mole) was obtained as a yellow-green compound, which was incapable of distillation under vacuum (Found: C, 45.73; H, 4.88. Mol.wt. in benzene, 544. $C_{22}H_{25}O_2Tl$ calcd.: C, 45.93; H, 4.52%. Mol.wt., 553.)

Hydrolysis of diethyl(diphenylphenoxysilyloxy)thallium with a 10% solution of H_2SO_4 followed by conversion of the resulting diethylthallium hydroxide into diethylthallium bromide yielded 0.13 g of the latter corresponding to 1 mole of product per mole of initial reactant. Diethyl(diphenylphenoxysilyloxy)thallium (0.58 g dissolved in 10 ml benzene) was also reacted with 10 ml of a 20% solution of NaOH by heating for 3 h on a water bath. The solvent was steam-distilled from the reaction mixture, acid was added to the resulting solution and phenol steam-distilled from it. The phenol was estimated as tribromophenol (0.32 g, 0.96 mole per mole of the reaction product).

Thermal decomposition of diethyl(triphenylgermylperoxy)thallium in cumene

A solution of the peroxide (1.04 g, 0.0017 mole) in 35 ml of cumene was placed in an ampoule, which was degassed and sealed under vacuum. The ampoule was heated for 35–40 h at 80°, cooled and opened. No measurable quantities of gas were observed. The solvent was distilled off at reduced pressure and the residue was found to be free from dicumyl. Diethyl(diphenylphenoxygermyloxy)thallium (0.99 g) of indeterminate melting point was extracted from the residue. (Found: C, 40.58; H, 3.59. Mol.wt. in benzene 591. $C_{22}H_{15}O_2TlGe$ calcd.: C, 40.13; H, 3.34%. Mol.wt., 598.) The IR spectrum of this compound exhibited a strong band near 1265 cm^{-1}, corresponding to the characteristic vibration of the phenoxy group.

The hydrolysis of diethyl(diphenylphenoxygermyloxy)thallium was studied in the presence of H_2SO_4 (2%). Thus, a solution of the product (0.36 g) in 10 ml of benzene, 10 ml of the acidic solution was added. A solution of KBr was added to the water layer and diethylthallium bromide (0.21 g, 1 mole per mole of product) was precipitated. From the benzene solution colourless crystals of diphenylphenoxygermyl hydroxide were obtained, m.p. 168°. (Found: C, 66.50; H, 5.49. Mol.wt. in benzene 303. $C_8H_{16}O_2Ge$ calcd.: C, 66.25; H, 4.91%. Mol.wt., 326.) The IR spectrum of this compound contained an absorption band at 1265 cm^{-1} corresponding to the phenoxy group and another at 3200–3300 cm^{-1} corresponding to the hydroxyl group.

Heating diphenylphenoxygermyl hydroxide (0.15 g) in toluene for 4 h at 120° resulted in the formation of colourless crystals of diphenylphenoxygermyl oxide (0.14

g) m.p. 182°. (Found: C, 65.61; H, 5.21. Mol. wt. in benzene 618. $C_{36}H_{30}O_3Ge$ calcd.: C, 66.05; H, 4.59%. Mol. wt., 659.)

Kinetic investigation of the thermal decomposition of diethyl(triphenylgermylperoxy)-thallium in benzene

A solution of the peroxide (0.02 mole) in benzene was degassed in a current of argon and placed in a special apparatus which was kept at a constant temperature within the range 55–70°, whose value did not vary by more than ±0.1°. At regular intervals samples were removed and estimated iodometrically for their peroxide oxygen content. From the experimental data a graph was plotted of the function $(1/c - 1/c_0) = f(t)$.

The thermal decomposition of the peroxide with various initial concentrations was studied at 60° in a similar manner, as were analogous reactions of the peroxide in the presence of equimolar quantities of the products of the rearrangement.

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