



Communication

First synthesis of cyclic organogermanium peroxides, 1,2,4,5,7,8-hexaoxa-3-germonanes

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ABSTRACT

First, previously unknown, cyclic organogermanium peroxides, 1,2,4,5,7,8-hexaoxa-3-germonanes, were synthesized by the reaction of 1,1'-dihydroperoxydi(cyclododecyl)peroxide with (di)alkyl(aryl)dihalogermanes. The new compounds have a higher tendency to undergo hydrolysis compared to silicon-containing analogs.

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1. Introduction

Nine-membered cyclic peroxides, 1,2,4,5,7,8-hexaoxananes (**A**) (Fig. 1), were synthesized for the first time in 1895 [1]. More than a hundred years later, in 2008, we prepared 1,2,4,5,7,8-hexaoxa-3-siloxanes (**B**) (Fig. 1), which are silicon-containing analogs of compounds **A** [2]. During the period of time between these publications, several tens of peroxides **A** were synthesized. The latter compounds are of interest for organic and analytical chemistry [3], materials science [4], and explosives manufacturing [5].

The present study is a continuation of our investigations on the chemistry of cyclic peroxides [2,6]. We synthesized organogermanium analogs of the structures **A** and **B**, 1,2,4,5,7,8-hexaoxa-3-germonanes (**C**) (Fig. 1), which are the first cyclic organogermanium peroxides. The aims of the present study were to develop procedures for the synthesis of these peroxides and evaluate their stability compared to Si analogs. The resulting peroxides were characterized by NMR spectroscopy.

Organogermanium peroxides are poorly studied. About 20 mono-, di-, three-, and tetraperoxygermanes were documented [7–11]. These compounds were synthesized by condensation of hydroperoxides or hydrogen peroxides with halogermanes [7–10], triphenylethoxygermane, or triphenylaminogermane [11]. The reaction of the sodium salt of *tert*-butyl hydroperoxide with triphenylgermanium bromide produced *tert*-butylperoxytriphenylgermanium [11].

2. Results and discussion

Earlier we have developed a procedure for the synthesis of Si-containing peroxides having the structure **B** based on the reaction of 1,1'-dihydroperoxydi(cycloalkyl)peroxides with (di)alkyl(aryl)dichlorosilanes in the presence of amines as acceptors for hydrogen chloride [2]. In the present study, we applied this procedure to the synthesis of structurally similar Ge-containing peroxides **C**. The latter compounds, 1,2,4,5,7,8-hexaoxa-3-germonanes (**3a–e**), were prepared by the reaction of 1,1'-dihydroperoxyperoxydi(cyclododecyl)peroxide (**1**) with (di)alkyl(aryl)dihalogermanes (**2a–e**) in the presence of triethylamine (Scheme 1 and Table 1).

Dichlorogermanes, unlike structurally similar dibromogermanes, are less active in this synthesis. The reactions of 1,1'-dihydroperoxyperoxydi(cyclododecyl)peroxide **1** with dibutylgermanium dichloride and methylphenylgermanium dichloride gave **3c** and **3d** in 8% and 11% yields, respectively. The analogous reaction of dibutylgermanium dibromide (**2c**) and methylphenylgermanium dibromide (**2d**) afforded the target peroxides **3c** and **3d** in higher yields (37% and 31%, respectively). Peroxide **3a** was synthesized in good yield (59%) only from sterically unhindered dimethyldichlorogermane (**2a**).

Experimentally, a key feature of the synthesis of **3** is that 1,1'-dihydroperoxyperoxydi(cyclododecyl)peroxide is initially mixed with (di)alkyl(aryl)dihalogermane followed by the addition of amine in an amount equivalent to hydrohalic acid that is released. When three components were mixed simultaneously, the target peroxides were obtained in low yield due, apparently, to the formation of strong

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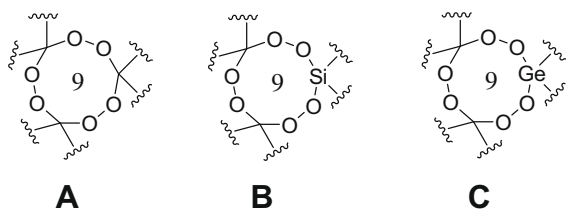


Fig. 1. Structures of 1,2,4,5,7,8-hexaoxananes (A), 1,2,4,5,7,8-hexaoxa-3-silonananes (B), 1,2,4,5,7,8-hexaoxa-3-germananes (C).

complexes of amine with 1,1'-dihydroperoxyperoxide (**1**) or (di)alkyl(aryl)dibromogermanes (**2**).

Attempts to synthesize 1,2,4,5,7,8-hexaoxa-3-germananes by the reactions of less stable peroxides, such as 1,1'-dihydroperoxydi(cyclohexyl)peroxide or 1,1'-dihydroperoxydi(cycloheptyl)peroxide, with dimethyldichloro- or diethyldibromogermane failed. Germanium peroxides that were formed in these reactions underwent considerable decomposition during the synthesis, which was not the case with silicon analogs. [2] Unlike silicon-containing cyclic peroxides, germanium peroxides more rapidly decompose during storage and are readily hydrolyzed with atmospheric moisture. The hydrolysis of organogermanium cyclic peroxides affords the starting 1,1'-dihydroperoxydi(cyclododecyl)peroxide **1** in high yield.

3. Experimental

Caution: Although we have encountered no difficulties in working with peroxides, precautions, such as the use of shields, fume hoods, and the avoidance of transition metal salts, heating and shaking, should be taken whenever possible.

The NMR spectra were recorded on Bruker WM-250 and AM-300 (250.13 and 300.13 MHz for ^1H ; 62.9 and 75.48 MHz for ^{13}C) spectrometers in CDCl_3 . Dialkyl(aryl)dihalogermanes (dimethylgermanium dichloride (**2a**) [12], diethylgermanium dibromide (**2b**) [13], dibutylgermanium dichloride [14], diphenylgermanium dibromide (**2e**) [15], and diphenylgermanium dichloride [15]) were synthesized according to known procedures. 1,1'-Dihydroperoxydi(cyclododecyl)peroxide (**1**) was synthesized according to the procedure described earlier [6]. Dibutylgermanium dibromide (**2c**) was prepared from dibutylgermanium dichloride in two steps involving the hydrolysis with a 20% aqueous NaOH solution followed by the treatment of the product with 48% aqueous hydrobromic acid by analogy with the known procedure [13,16]. Methylphenylgermanium dibromide (**2d**) was prepared by the reaction of triphenylgermanium chloride with MeMgBr followed by the treatment of methyltriphenylgermanium that was formed in the first step with bromine by analogy with the known procedure [17]. Methylphenylgermanium dichloride was

Table 1
Structures and yields of 1,2,4,5,7,8-hexaoxa-3-germananes (**3a–e**).^a

Structure	3a	3b	3c^b	3d^c	3e
Total reaction time (h)	4	7	20	20	20
Yield (%)	59	43	37	31	41

^a Reaction conditions: A mixture of 1,1'-dihydroperoxydi(cyclododecyl)peroxide **1** (0.1 g, 0.23 mmol) and disubstituted dihalogermane **2a–e** (0.35 mmol) in anhydrous THF (6 mL) was allowed to stand for 1 h. Then a solution of triethylamine (0.71 mmol) in anhydrous THF (2 mL) was added, and the reaction mixture was stirred at room temperature for 4–20 h.

^b The reaction with dibutylgermanium dichloride afforded **3c** in 8% yield.

^c The reaction with methylphenylgermanium dichloride gave **3d** in 11% yield.

prepared from methylphenylgermanium dibromide (**2d**) in two steps involving the hydrolysis with a 20% aqueous NaOH solution followed by the treatment of the product with 34% aqueous hydrochloric acid by analogy with the known procedure [13,16]. Elemental analysis of germanium was calculated from the mass of germanium oxide after burning of organogermanium peroxides under oxygen atmosphere in the presence of crushed quartz [18].

3.1. Dibutylgermanium dibromide (**2c**)

^1H NMR (250.13 MHz, CDCl_3), δ : 0.93 (t, 6H, CH_3 , $J = 6.7$ Hz), 1.37–1.82 (m, 12H, CH_2). ^{13}C NMR (62.9 MHz, CDCl_3), δ : 12.7 (CH_3), 24.8, 26.4, 27.8 (CH_2). Anal. Calc. for $\text{C}_8\text{H}_{18}\text{Br}_2\text{Ge}$: C, 27.72; H, 5.23; Br, 46.10; Ge, 20.95. Found: C, 27.91; H, 5.01; Br, 46.27; Ge, 20.48%.

3.2. Methylphenylgermanium dibromide (**2d**)

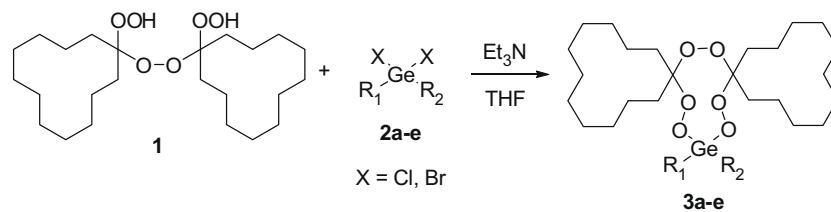
^1H NMR (250.13 MHz, CDCl_3), δ : 1.71 (s, 3H, CH_3), 7.56 (br.s., 3H, CH), 7.78 (br.s., 2H, CH). ^{13}C NMR (62.9 MHz, CDCl_3), δ : 11.7 (CH_3), 128.9, 131.6, 131.7, 136.9 (CH_2). Anal. Calc. for $\text{C}_7\text{H}_8\text{Br}_2\text{Ge}$: C, 25.90; H, 2.48; Br, 49.24; Ge, 22.37. Found: C, 25.56; H, 2.74; Br, 49.11; Ge, 22.56%.

3.3. Methylphenylgermanium dichloride

^1H NMR (250.13 MHz, CDCl_3), δ : 1.44 (s, 3H, CH_3), 7.54 (m, 3H, CH), 7.76 (m, 2H, CH). ^{13}C NMR (62.9 MHz, CDCl_3), δ : 8.8 (CH_3), 129.0, 131.7, 131.8, 136.3 (CH_2). Anal. Calc. for $\text{C}_7\text{H}_8\text{Cl}_2\text{Ge}$: C, 35.68; H, 3.42; Cl, 30.09; Ge, 30.81. Found: C, 35.77; H, 3.36; Cl, 30.14; Ge, 30.69%.

3.4. Procedure for the synthesis of 1,2,4,5,7,8,3-hexaoxagermananes (**3a–e**)

A mixture of 1,1'-dihydroperoxydi(cyclododecyl)peroxide **1** (0.1 g, 0.23 mmol) and (di)alkyl(aryl)dihalogermane **2a–e** (0.35 mmol) in anhydrous THF (6 mL) was allowed to stand for



a: X = Cl, $\text{R}_1 = \text{R}_2 = \text{Me}$; **b:** X = Br, $\text{R}_1 = \text{R}_2 = \text{Et}$; **c:** X = Br, $\text{R}_1 = \text{R}_2 = \text{Bu}$;

d: X = Br, $\text{R}_1 = \text{Me}$, $\text{R}_2 = \text{Ph}$; **e:** X = Br, $\text{R}_1 = \text{R}_2 = \text{Ph}$

Scheme 1. Synthesis of 1,2,4,5,7,8-hexaoxa-3-germananes (**3a–e**).

1 h. Then a solution of triethylamine (0.71 mmol) in anhydrous THF (2 mL) was added. The reaction mixture was stirred at room temperature for 4–20 h. The precipitate was filtered off, and the filtrate was concentrated to 1/5 of the initial volume. Then methanol (15 mL) was added, the reaction mixture was cooled to -20°C , and the crystals of **3a–e** that formed were filtered off and washed with methanol (5×1 mL). Compounds **3a–e** were dried *in vacuo* (10 mm Hg) at room temperature for 1 h.

3.5. 29,29-Dimethyl-13,14,27,28,30,31-hexaoxa-29-germadispiro [11.2.11.5]hentriacontane (**3a**)

M.p. (MeOH) = $178\text{--}180^{\circ}\text{C}$. ^1H NMR (250.13 MHz, CDCl_3), δ : 0.61–0.82 (m, 6H, CH_3), 1.24–1.92 (m, 44H, CH_2). ^{13}C NMR (75.48 MHz, CDCl_3), δ : -2.0 (CH_3), 19.5, 22.0, 22.3, 26.1, 26.2, 26.5 (CH_2), 112.7 (C). Anal. Calc. for $\text{C}_{26}\text{H}_{50}\text{GeO}_6$: C, 58.78; H, 9.49; Ge, 13.67. Found: C, 58.66; H, 9.11; Ge, 13.07%.

3.6. 29,29-Diethyl-13,14,27,28,30,31-hexaoxa-29-germadispiro [11.2.11.5]hentriacontane (**3b**)

M.p. (MeOH) = $154\text{--}156^{\circ}\text{C}$. ^1H NMR (300.13 MHz, CDCl_3), δ : 1.12–1.92 (m, 54H, CH_2 , CH_3). ^{13}C NMR (75.48 MHz, CDCl_3), δ : 7.4, 7.7 (CH_2CH_3), 19.4, 21.9, 22.2, 26.0, 26.2, 26.6 (CH_2), 112.3 (C). Anal. Calc. for $\text{C}_{28}\text{H}_{54}\text{GeO}_6$: C, 60.12; H, 9.73; Ge, 12.98. Found: C, 59.87; H, 9.52; Ge, 13.01%.

3.7. 29,29-Dibutyl-13,14,27,28,30,31-hexaoxa-29-germadispiro [11.2.11.5]hentriacontane (**3c**)

M.p. (MeOH) = $116\text{--}121^{\circ}\text{C}$. ^1H NMR (300.13 MHz, CDCl_3), δ : 0.85–0.94 (m, 6H, CH_3), 1.15–1.86 (m, 56H, CH_2). ^{13}C NMR (75.48 MHz, CDCl_3), δ : 13.6, 19.5, 21.9, 22.3, 25.3, 25.6, 26.1, 26.2 (CH_2 , CH_3), 112.0 (C). Anal. Calc. for $\text{C}_{32}\text{H}_{62}\text{GeO}_6$: C, 62.45; H, 10.15; Ge, 11.80. Found: C, 62.27; H, 9.94; Ge, 11.47%.

3.8. 29-Methyl-29-phenyl-13,14,27,28,30,31-hexaoxa-29-germadispiro [11.2.11.5]hentriacontane (**3d**)

M.p. (MeOH) = $106\text{--}108^{\circ}\text{C}$. ^1H NMR (300.13 MHz, CDCl_3), δ : 0.77–1.02 (m, 3H, CH_3), 1.23–2.02 (m, 44H, CH_2), 7.25–7.77 (m, 5H, CH). ^{13}C NMR (75.48 MHz, CDCl_3), δ : -4.1 (CH_3), 19.3, 19.5, 21.9, 22.2, 26.0, 26.2, 26.4, 26.5 (CH_2), 112.6 (OCO), 128.5, 131.1, 132.7, 133.9 (Car). Anal. Calc. for $\text{C}_{31}\text{H}_{52}\text{GeO}_6$: C, 62.75; H, 8.83; Ge, 12.24. Found: C, 62.53; H, 8.57; Ge, 12.04%.

3.9. 29,29-Diphenyl-13,14,27,28,30,31-hexaoxa-29-germadispiro [11.2.11.5]hentriacontane (**3e**)

M.p. (MeOH) = $187\text{--}189^{\circ}\text{C}$. ^1H NMR (300.13 MHz, CDCl_3), δ : 1.18–2.0 (m, 44H, CH_2), 7.25–7.80 (m, 10H, CH).

(75.48 MHz, CDCl_3), δ : 19.3, 19.5, 21.9, 22.2, 26.0, 26.2, 26.7 (CH_2), 112.8 (OCO), 128.6, 130.9, 131.2, 134.6 (Car). Anal. Calc. for $\text{C}_{36}\text{H}_{54}\text{GeO}_6$: C, 65.97; H, 8.30; Ge, 11.08. Found: C, 65.79; H, 8.02; Ge, 11.24%.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.02.005.

References

- [1] R. Wolffenstein, Chem. Ber. 28 (1895) 2265–2269.
- [2] A.O. Terent'ev, M.M. Platonov, A.I. Tursina, V.V. Chernyshev, G.I. Nikishin, J. Org. Chem. 73 (2008) 3169–3174.
- [3] (a) P.L. Story, D.D. Denson, C.E. Bishop, B.C. Clark Jr., J.-C. Farine, J. Am. Chem. Soc. 90 (1968) 817–818; (b) J.R. Sanderson, K. Paul, P.R. Story, D.D. Denson, J.A. Alford, Synthesis (1975) 159–161; (c) F. Dubnikova, R. Kosloff, J. Almog, Y. Zeiri, R. Boese, H. Itzhaky, A. Alt, E. Keinan, J. Am. Chem. Soc. 127 (2005) 1146–1159; (d) C. Denekamp, L. Gottlieb, T. Tamiri, A. Tsoglin, R. Shilav, M. Kapon, Org. Lett. 7 (2005) 2461–2464; (e) J. Oxley, J. Smith, J. Brady, F. Dubnikova, R. Kosloff, L. Zeiri, Y. Zeiri, Appl. Spectrosc. 62 (2008) 906–915.
- [4] (a) B. Fisher, J. Meijer, R. Hendrik, V.D. Berg, J. Nuysink (AKZO NOBEL N.V.), US Patent 0,162,436, 2004; (b) S. Wei-Chen, W. Jian-Yi, S. Guo-Rong, H. Zhi-Ming, W. Zhi-Xue, J. Appl. Polym. Sci. 94 (2004) 1035–1042.
- [5] R. Meyer, Explosives, Verlag Chemie, Weinheim New York, 1977.
- [6] A.O. Terent'ev, M.M. Platonov, E.J. Sonneveld, R. Peschar, V.V. Chernyshev, Z.A. Starikova, G.I. Nikishin, J. Org. Chem. 72 (2007) 7237–7243.
- [7] A.G. Davies, C.D. Hall, J. Chem. Soc. (1959) 3835–3838.
- [8] N.P. Sluchevskaya, V.A. Yablokov, N.V. Yablokova, Yu.A. Alexandrov, J. Gen. Chem. USSR (Engl. Transl.) 46 (1976) 2599; N.P. Sluchevskaya, V.A. Yablokov, N.V. Yablokova, Yu.A. Alexandrov, Zh. Obshch. Khim. 46 (1976) 2724–2726.
- [9] N.P. Sluchevskaya, V.A. Yablokov, N.V. Yablokova, J. Gen. Chem. USSR (Engl. Transl.) 47 (1977) 1417–1419; N.P. Sluchevskaya, V.A. Yablokov, N.V. Yablokova, Zh. Obshch. Khim. 47 (1977) 1544–1548.
- [10] R.L. Dannley, G.C. Farrant, J. Org. Chem. 34 (1969) 2428–2432.
- [11] A. Rieche, J. Dahlmann, Liebigs Ann. Chem. 675 (1964) 19–35.
- [12] E. Rockow, J. Am. Chem. Soc. 69 (1947) 1729–1731.
- [13] E.A. Flood, J. Am. Chem. Soc. 54 (1932) 1663–1667.
- [14] E.R. Ruckel, L.S. Wang (Arizona Chemical Company), US patent 4113653.
- [15] C.A. Kraus, C.L. Brown, J. Am. Chem. Soc. 52 (1930) 3690–3696.
- [16] H.H. Anderson, J. Am. Chem. Soc. 73 (1951) 5440–5441.
- [17] O.H. Jonson, D.M. Harris, in: Therald Moellar (Ed.), Inorganic Syntheses, vol. 5, McGraw-Hill, New York, 1957, p. 74.
- [18] E.E. Gel'man, Dr. Thesis, A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences, 1972, p. 341.