

**Registry No.**—Dimethyl acetylenedicarboxylate, 762-42-5; benzene, 71-43-2; naphthalene, 91-20-3; VI, 19981-73-8; VII, 19988-65-9; VIII, 19988-66-0; VIII (hydrogenated), 19981-74-9; IX, 19981-75-0; XI, 19988-67-1; dimethyl cyclooctatetraene-1,2-carboxylate, 15956-91-9; cyclooctatetraene-1,2-dicarboxylic acid, 13753-01-0; dimethyl hydroxymethylfumarate, 19988-68-2; dimethyl cyclohexylfumarate, 19988-69-3; benzocyclooctene-7,8-dicarboxylic anhydride, 19981-78-3; dimethyl 1-naphthalenesuccinate, 19981-79-4; dimethyl 2-naphthalenemaleate, 19988-70-6; dimethyl 2-naphthalenefumarate, 19988-71-7; *trans*-

acenaphthene-1,2-dicarboxylic acid (di-*N*-benzylamide), 19988-72-8; naphthalene-2,3-dicarboxylic acid (di-*N*-benzylamide), 19981-80-7; naphthalene-2,3-dicarboxylic acid (*N*-benzylimide), 20013-26-7.

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## The Synthesis and Properties of Germanium Peroxides and Hydroperoxides<sup>1</sup>

RALPH L. DANNLEY AND GEORGE C. FARRANT

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

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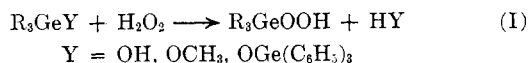
Triphenylgermyl, diphenyl-*p*-trifluoromethylphenylgermyl, diphenyl-*p*-methoxyphenylgermyl, and tricyclohexylgermyl hydroperoxides and bis(diphenyl-*p*-trifluoromethylphenylgermyl) peroxide have been synthesized from the corresponding organogermanium halides, hydroxides, oxides, methoxides, or amines. The infrared, pmr, and mass spectra are consistent with the proposed structures. Treatment of all of the germyl hydroperoxides or peroxides except *p*-methoxyphenyldiphenylgermyl hydroperoxide with hydrogen chloride yielded the corresponding chlorides in essentially quantitative yields. The *p*-methoxyphenyl group was partially cleaved from germanium upon treatment with hydrogen chloride to produce diphenylgermanium dichloride and anisole.

As a continuation of the studies of the hydroperoxides and peroxides of the group IVb elements,<sup>2-5</sup> representative germanium derivatives of this type have now been synthesized and their chemical and physical properties investigated.

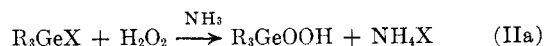
Although several unsymmetrical peroxides containing the GeOOC structure<sup>6,7</sup> and three bisgermyl peroxides have been described,<sup>7-9</sup> the corresponding hydroperoxides had not been synthesized until the preliminary announcement of the preparation of triphenylgermyl hydroperoxide.<sup>5</sup> The present work was undertaken to synthesize a series of germanium hydroperoxides, add to the list of known bisgermyl peroxides, and to determine the physical and chemical properties of these compounds.

### Results

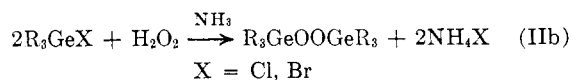
The hydroperoxides were synthesized by either a direct nucleophilic displacement of a hydroxy or methoxy group by 98% hydrogen peroxide (method I)



or by displacement of a halide by hydrogen peroxide in the presence of anhydrous ammonia (method IIa).



The bisgermyl peroxides were synthesized by the reaction of a stoichiometric amount of hydrogen peroxide with a triarylhalogermane in the presence of ammonia (method IIb). The yields, methods of synthesis, and analyses are given in Table I.



The structures of the peroxidic compounds were confirmed by physical methods as well as by elemental and active oxygen analyses. The infrared spectra of the hydroperoxides show a strong absorption in the 3570–3200-cm<sup>-1</sup> region, indicative of the OH structure. The exchangeable proton in the pmr absorption spectra of the hydroperoxides in deuteriochloroform, listed in Table II, absorbs at very low-field strength, *ca.* δ 7.50. This is similar to the δ 7.8 value for the hydroperoxy proton of *t*-butyl hydroperoxide. Since the hydroxy proton of triphenylgermanol absorbs at δ 1.43 in deuteriochloroform, the low downfield absorptions of the triphenylgermyl hydroperoxide indicates that its exchangeable proton must be attached to the highly electronegative peroxy unit.

The molecular weight of triphenylgermyl hydroperoxide determined by vapor phase osmometry, employing benzene as solvent, was found to be 359 ± 12 for a 0.054 *M* solution, 325 ± 12 for a 0.017 *M* solution, and 323 ± 13 for a 0.0060 *M* solution. Since the molecular formula requires 336, these results indicate that there is a slight degree of association of the hydroperoxide in this solvent as the concentration is increased.

(1) (a) Supported by the U. S. Army Research Office (Durham) through Grant No. DA-ARO (D)-31-124-G720. (b) Taken in part from the dissertation of G. C. Farrant submitted in Jan. 1968 to the Graduate School of Case Western Reserve University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (c) Presented in part at the first Central Regional Meeting of the American Chemical Society, Akron, Ohio, May 10, 1968.

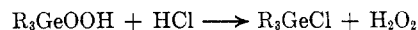
(2) R. L. Dannley and G. Jalios, *J. Org. Chem.*, **30**, 2417 (1965).  
 (3) R. L. Dannley and G. Jalios, *ibid.*, **30**, 3848 (1965).  
 (4) R. L. Dannley and W. A. Aue, *ibid.*, **30**, 3845 (1965).  
 (5) R. L. Dannley and G. Farrant, *J. Amer. Chem. Soc.*, **88**, 627 (1966).  
 (6) A. G. Davies and C. D. Hall, *J. Chem. Soc.*, 3835 (1959).  
 (7) A. G. Davies and C. D. Hall, *Chem. Ind. (London)*, 1895 (1958).  
 (8) A. Rieche and J. Dahlmann, *Angew. Chem.*, **73**, 494 (1961).  
 (9) A. Rieche and J. Dahlmann, *Ann.*, **675**, 19 (1964).

TABLE I  
 PREPARATION AND ANALYSIS OF ORGANOGermanium HYDROPEROXIDES AND PEROXIDES

Registry no.	Product	Starting reagent	Method of prepn	% yield	Mp, °C (n <sub>D</sub> <sup>20</sup> )	Recrystn solvent	Calcd, %				Found			
							C	H	Ge	Active oxygen	C	H	Ge	Active oxygen
5274-38-4	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeOOH	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeCl	IIa	60	137.5-138.0	Ether	64.17	4.79	17.92	4.76	64.39	4.76	17.91	4.75
	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeOOH	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeBr	IIa	55	137.5-138.0	Ether								
	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeOOH	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeOH	I	60	137.5-138.0	Ether								
	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeOOH	[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Ge] <sub>2</sub> O	I	65	137.5-138.0	Ether								
19987-82-7	<i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeOOH	<i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeCl	IIa	42	81.0-81.5	Ether	56.40	3.74	17.92	3.90	56.33	3.97	17.91	3.96
19987-83-8	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeOOH	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeOCH <sub>3</sub>	I	98	(1.6237)		62.40	4.95	19.75	4.37	62.28	5.10	19.54	4.32
19987-84-9	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeOOH	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeCl	IIa	65	180-182 dec	Pentane	60.70	9.65	20.40	4.35	61.05	9.76	20.16	4.39
5695-57-8	[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeO] <sub>2</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeCl	IIb	60	147-148	Pentane-ether (1:1)	67.22	4.70	22.60	2.50	67.45	4.72	22.40	2.45
19987-86-1	[ <i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeO] <sub>2</sub>	<i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeCl	IIb	57	134-137	Pentane-ether (1:1)	58.95	3.64		2.07	58.89	3.71		2.05

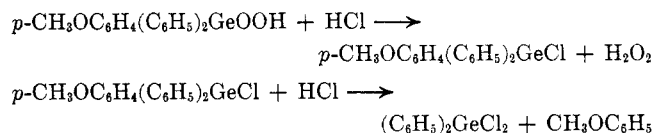
The mass spectrum of triphenylgermyl hydroperoxide taken at 70 eV shows peaks at 334, 336, 337, 338, and 340 mass units, corresponding to the molecular ions expected from the five stable isotopes of germanium.

**Reaction with Hydrogen Chloride.**—All of the hydroperoxides, except diphenyl-*p*-methoxyphenylgermyl hydroperoxide, reacted with hydrogen chloride at 25° within 10 min to produce the corresponding triorgano-germanium chloride and hydrogen peroxide in better than 98% yield (glpc). There was no rearrangement accompanying this reaction and it therefore obeyed the given stoichiometric equation. No diphenylger-



manium dichloride or benzene was found in the acid-treated solutions although yields as low as 0.1 mol % could be detected.

Diphenyl-*p*-methoxyphenylgermyl hydroperoxide, on the other hand, when similarly treated with hydrogen chloride, formed diphenylgermanium dichloride and anisole as well as the monochloride in roughly equal amounts. The fact that neither *p*-methoxyphenol nor phenol were formed means that the primary reaction involved the displacement of the germanium oxygen bond to form the monochloride. A secondary reaction involved the cleavage of the anisyl group from either the newly formed monochloride or from the unreacted hydroperoxide. This contention is supported by the fact that high yields of anisole and diphenyldichloro-germane were formed when a 0.05 *M* solution of the monochloride was treated with anhydrous hydrogen chloride under the same conditions. All attempts to



convert this hydroperoxide into its monochloride by reducing the contact time with hydrogen chloride resulted either in incomplete conversion to the monochloride or a substantial amount of cleavage of the anisyl group. Since the *p*-methoxyphenyl group has been shown to cleave some 400-500 times as readily as the phenyl group in the reaction of aryltriethylgermanes with mineral acids,<sup>10</sup> the cleavage of the anisyl group in the present system is not surprising.

The symmetrical bisperoxides prepared during this study also formed the triorganochloro-germanes in better than 97% yield when treated with hydrogen chloride. As in the case of hydroperoxides, no rearrangement occurred during the course of the reaction. These results corroborate the findings of Rieche and Dahlmann,<sup>9</sup> who found that the unsymmetrical carbon germanium peroxides undergo primary oxygen-metal cleavage with hydrogen chloride and not the acid-catalyzed heterolysis of the peroxy bond.

### Discussion

The syntheses of the germyl hydroperoxides from hydrogen peroxide and the germanols, germanium oxides, or germanium methoxides are probably simple nucleophilic displacements. The resultant equilibria

(10) (a) C. Earborn and K. C. Pande, *J. Chem. Soc.*, 297 (1961); (b) C. Earborn and K. C. Pande, *ibid.*, 5082 (1961); (c) C. Earborn and K. C. Pande, *ibid.* 1566 (1960).

TABLE II  
 THE PMR SPECTRAL ABSORPTIONS OF ORGANGERMYL HYDROPEROXIDES<sup>a</sup>

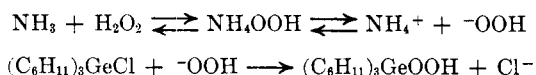
Compd	Hydroperoxy proton	Aromatic protons	Aliphatic protons
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeOOH	7.64 (S)	7.20-7.85 (M)	
CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeOOH	7.50 (S)	6.55-7.60 (M)	3.79 (S)
CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> GeOOH	7.70 (S)	6.55-7.60 (M)	
(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> GeOOH	7.24 (S)		1.0-2.4 (M)

<sup>a</sup> The spectra were taken on a Varian A-60 nuclear magnetic resonance spectrometer. The solvent was deuteriochloroform (5-10% solutions). The chemical shifts were measured in parts per million from internal TMS: S = singlet, M = multiplet.

are shifted in the proper direction by the excess of hydrogen peroxide, as well as its lower volatility compared with the water or methanol, which is preferentially removed by evaporation. When both the starting material and the final product are liquids, as in the case of the diphenyl-*p*-methoxyphenylgermyl derivative, Table II, the hydroperoxide can be obtained in high yield. However, when the reactants and products are solids, good contact with the hydrogen peroxide is not achieved and the hydroperoxide is of low purity and must be purified by recrystallization. This reduces the yield and method II is preferred.

The mechanism of the formation of triarylgermyl hydroperoxides from the corresponding triarylhalogermane using ammonia as the catalyst (method IIa) is possibly identical with the analogous formation of triorganosilyl hydroperoxides.<sup>2</sup> In the absence of hydrogen peroxide, triarylgermanium amines are rapidly and quantitatively formed. Subsequent displacement of the amide ion by hydrogen peroxide or its anion would lead to the formation of the hydroperoxide. Displacement of the amide ion by triarylgermyl hydroperoxide or its anion would lead to the formation of the symmetrical bisperoxide (method IIb). Undoubtedly there were other reactions occurring in solution many of which were reversible in nature. The position of equilibrium in these reactions depends upon both the electronic and steric effects in the molecules. Hence, in order to prepare a specific hydroperoxide or peroxide different reaction conditions often had to be used.

Although the order of addition of hydrogen peroxide and ammonia was unimportant for the successful synthesis of the triarylgermyl hydroperoxides or peroxides, it was extremely important for the preparation of tricyclohexylgermyl hydroperoxide. When ammonia was bubbled into an ethereal solution of tricyclohexylchlorogermane at 0°, the precipitation of ammonium chloride was very slow and was complete only after 15 or 20 min. However, when the reaction was carried out in the presence of hydrogen peroxide, the precipitation of ammonium chloride was immediate. This indicates that the main reaction sequence involved the nucleophilic displacement of the chloride by the hydroperoxy anion according to the given equations. The



formation of the germyl amine as an intermediate is not excluded but it can only be a competing reaction. The small steric requirements of the peroxy anion make it the species likely to attack the germyl chloride substituted by the bulky cyclohexyl groups. Steric effects of the alkyl groups have been proved to be of principle importance in other reactions of germyl derivatives. Thus triethyl- and tri-*n*-propylgermanol lose water

readily to form the symmetrical oxide while the triisopropylgermanol loses water only slowly below 200°<sup>11</sup> and tricyclohexylgermanol does not form the symmetrical oxide.

All efforts to prepare diphenyl-*p*-methoxyphenylgermyl hydroperoxide from the corresponding germanium chloride using method II met with failure. It is likely that the germanium amine formed, for ammonium chloride precipitated rapidly and quantitatively when the chloride was treated with ammonia. Apparently the hydroperoxide was formed, but underwent a base-catalyzed decomposition prior to its isolation, for only oils of limited active oxygen could be obtained. However, it was found that diphenyl-*p*-methoxyphenylgermyl hydroperoxide could be prepared pure and in very high yield by displacing the methoxy group of the corresponding methoxide with hydrogen peroxide (method I). The hydroperoxide prepared in this manner contained more than 95% of the theoretical active oxygen content. Attempts to crystallize the material always resulted in oils of decreased active oxygen content. However, the material gave the correct elemental analysis, and its infrared and pmr spectra were consistent with the above structural assignment (Table II).

### Experimental Section

A number of germanium-containing reagents and reference compounds were prepared and are listed in Table III. The mono-substituted tri-arylhalogermanes were prepared by addition of an arylmagnesium bromide to diphenyldichlorogermane. Since the resulting products were found to be mixtures of the corresponding germyl bromides and chlorides, conversion into the pure halide was achieved by hydrolyzing each crude reaction mixture to the germyl hydroxide or oxide and then treating this with either hydrogen chloride or hydrogen bromide.

**Organohalogermanes.**—Triphenylchlorogermane, triphenylbromogermane, diphenyldichlorogermane, and tricyclohexylchlorogermane were purchased from either Metallomer Laboratories or Alfa Inorganics, and were used without further purification. The unsymmetrically substituted organohalogermanes prepared during this study were synthesized either by a Grignard arylation of an appropriate diphenyldichlorogermane or phenyltrichlorogermane or reaction of a chloroform solution of the corresponding organogermanium hydroxide (or oxide) with hydrogen chloride or hydrogen bromide. Since the Grignard reaction was most often used, the synthesis of diphenyl-*p*-trifluoromethylchlorogermane will be described. It also illustrates the method used for the synthesis of the other organohalogermanes.

**Diphenyl-*p*-trifluoromethylphenylchlorogermane.**—*p*-Trifluoromethylphenylmagnesium bromide was prepared by adding *p*-trifluoromethylbromobenzene (16.9 g, 75 mmol) to magnesium turnings (2.00 g, 82 mmol) in anhydrous ether (100 ml). The solution separated into two phases, both of which were slowly added to a boiling solution of diphenyldichlorogermane (22.2 g, 76 mmol) in dry toluene (600 ml). The Grignard solution was added at such a rate that the ether distilled without flooding the condenser. When all of the Grignard reagent had been added and the ether removed by distillation, the resulting purple solution was refluxed at 110° for 18 hr. The solution was concen-

(11) H. H. Anderson, *J. Amer. Chem. Soc.*, **75**, 814 (1953).

TABLE III  
 PROPERTIES AND ELEMENTAL ANALYSES OF ORGANOGermanium REFERENCE COMPOUNDS

Compd	Registry no.	Mp, °C	Bp (mm), °C	Calcd, %				Found, %			
				C	H	Ge	Cl or Br	C	H	Ge	Cl or Br
$p\text{-CF}_3\text{C}_6\text{H}_4(\text{C}_6\text{H}_5)_2\text{GeCl}$	19987-87-2	54-55	150-159 (0.40)	55.58	3.47	17.82	7.52	55.80	3.52	18.08	7.52
$p\text{-CF}_3\text{C}_6\text{H}_4(\text{C}_6\text{H}_5)_2\text{GeBr}$	19987-88-3	67.0-68.5		50.20	3.13	16.10	17.71	50.24	2.81	15.97	17.93
$p\text{-CH}_3\text{OC}_6\text{H}_4(\text{C}_6\text{H}_5)_2\text{GeCl}$	19987-89-4	80.0-81.5	185-190 (0.025)	61.82	4.65	19.68	9.35	61.65	4.52	19.41	9.61
$p\text{-CH}_3\text{OC}_6\text{H}_4(\text{C}_6\text{H}_5)_2\text{GeBr}$	19987-90-7	75-76		55.30	4.15	17.55	19.29	55.30	4.27	17.32	19.22
$p\text{-CH}_3\text{OC}_6\text{H}_4(\text{C}_6\text{H}_5)_2\text{GeOH}$	19987-91-8	77.5-80.5		65.00	5.17	20.68		64.98	5.20	20.47	
$[p\text{-CH}_3\text{OC}_6\text{H}_4(\text{C}_6\text{H}_5)_2\text{Ge}]_2\text{O}$	19987-92-9	107		67.14	5.02	21.30		67.41	5.07	21.14	
$[p\text{-CF}_3\text{C}_6\text{H}_4(\text{C}_6\text{H}_5)_2\text{Ge}]_2\text{O}$	19987-93-0	133		60.30	3.59	19.15		60.51	3.72	18.91	
$p\text{-CH}_3\text{OC}_6\text{H}_4(\text{C}_6\text{H}_5)_2\text{GeOCH}_3^a$	19987-94-1		185-187 (0.20)	65.61	5.65	19.81		65.64	5.62	19.65	

<sup>a</sup> n<sub>D</sub><sup>20</sup> 1.6062.

trated to approximately 200 ml and then filtered. The semisolid precipitate was dissolved in 200 ml of 3 N hydrochloric acid. The acidic solution was extracted with two 100-ml portions of benzene and the extracts were combined with the filtrate from the previous step. When the solvents were removed from the combined solution by evaporation under reduced pressure, a brown oil remained which was shown by glpc to contain diphenyl-*p*-trifluoromethylphenylchlorogermane and diphenyl-*p*-trifluoromethylphenylbromogermane as the two major components in a ratio of approximately 1:2. The crude material was then dissolved in ether (200 ml) and ammonia bubbled under the surface until no more ammonium halide precipitated. The solution was washed two times with 100-ml portions of water and the organic phase was separated and dried over magnesium sulfate. The dried solution was filtered, dried with magnesium sulfate, and the solution then was treated with anhydrous hydrogen chloride to convert the organogermanol into the organochlorogermane. The solvent was removed under vacuum, leaving a dark brown oil (20 g) which was shown by glpc to be the desired product contaminated with approximately 10% diphenyldichlorogermane. The crude liquid was distilled at reduced pressure through a short-path distillation column and the fraction boiling at 150-159° (0.40 mm) (17.2 g, 56% yield) solidified upon standing to give white crystals which melted at 54-55°. The infrared spectrum showed a band at 829 cm<sup>-1</sup>, indicating *para* substitution.

**Organogermanols.**—The organogermanols were prepared by the following general procedure. Into a solution of ether (100 ml) and the triorganohalogermane (2.5 mmol) was introduced ammonia gas until no more ammonium halide precipitated. The solution was then washed three times with 20-ml portions of water and the organic phase separated and dried over magnesium sulfate. The ether was removed under reduced pressure and the residue then recrystallized. Triphenylgermanol, when recrystallized from hexane-ether, had mp 134° (lit.<sup>12</sup> mp 132.2°). Tricyclohexylgermanol, when recrystallized from heptane, had mp 176° (lit.<sup>13</sup> mp 176-177°).

**Organogermanium Oxides.**—The triorganogermanium oxides were synthesized according to the following procedure. To heptane (100 ml) was added phosphorus pentoxide (0.30 g) and 5 mmol of the triorganogermanol. The mixture was stirred for 1 hr at 60°. The liquid was decanted from the solid phosphorus pentoxide and the solvent removed from the solution under vacuum. The residue was recrystallized several times until a constant melting point was obtained. Triphenylgermanium oxide had mp 183-184° (lit.<sup>14</sup> mp 185-187°).

**Diphenyl-*p*-methoxyphenylmethoxygermane.**—Diphenyl-*p*-methoxyphenylbromogermane (1.0 g, 2.5 mmol) was dissolved in an ether solution (100 ml) containing anhydrous methanol (1.0 ml). Anhydrous ammonia gas was bubbled under the surface of the solution for 2 min. The solution was filtered and the solvent removed from the filtrate under reduced pressure leaving a clear liquid (0.88 g, 99% yield) which was the desired product. Since the methoxide is very sensitive to moisture it must be stored in a desiccator. The pmr spectrum consisted of three absorption peaks—a multiplet in the aromatic region at -6.93-7.35 ppm, a singlet at -3.70 ppm due to the methoxy portions on the aromatic rings, and a singlet at -3.62 ppm due to the methoxy protons attached to germanium—in the expected ratio of 14:3:3.

**Preparation of a Hydroperoxide. Method I.**—Triphenylbromogermane (2.0 g, 5.2 mmol) was dissolved in anhydrous ether (200 ml) to which 98% hydrogen peroxide (2.0 ml, 85 mmol) had been added. The solution was stirred for several minutes at 0° and then anhydrous ammonia was bubbled under the surface for 30 sec, precipitating ammonium bromide. The reaction was quenched with distilled water (30 ml). The organic phase was washed twice with 30-ml portions of water and dried over magnesium sulfate for 10 min. The solution was filtered and the filtrate evaporated under vacuum in a rotary evaporator to give white crystalline triphenylgermyl hydroperoxide (1.1 g, 55% yield). After two recrystallizations from diethyl ether, crystals which melted at 137.5-138° were obtained.

**Method IIa.**—Diphenyl-*p*-methoxyphenylmethoxygermane (2.0 g, 5.5 mmol) was placed in a glass tube closed at one end, together with anhydrous ether (20 ml) and a small magnetic stirring bar. To the solution was added 98% hydrogen peroxide

(12) C. A. Kraus and L. S. Foster, *J. Amer. Chem. Soc.*, **49**, 457 (1927).(13) O. H. Johnson and W. H. Nebergall, *ibid.*, **71**, 1720 (1949).(14) A. G. Brovic, *ibid.*, **77**, 5059 (1955).

(2.0 ml, 85 mmol). The mixture was stirred rapidly and a stream of dry nitrogen was allowed to pass over the top of the open tube until most of the ether had evaporated. The tube was then connected to a vacuum line and the pressure was slowly reduced to 0.20 mm for 4 hr. There remained at the end of this treatment 2.0 g (99% yield) of a clear viscous oil, which was diphenyl-*p*-methoxyphenylgermyl hydroperoxide.

**Preparation of a Bisgermyl Peroxide. Method Iib.**—Diphenyl-*p*-trifluoromethylphenylchlorogermane (2.0 g, 4.8 mmol) was dissolved in a solution of anhydrous ether (200 ml) and

hydrogen peroxide (0.289 g, 8.5 mmol). At 25° anhydrous ammonia gas was bubbled under the surface for 2 min, and the mixture stirred for another 5 min. The mixture was then filtered through a medium fritted-glass filter and the solvent removed from the filtrate. There remained a clear viscous oil (6.65 g) which was dissolved in 10 ml of pentane and cooled to -20°. The white precipitate which formed (3.70 g, 57% yield), after collection by filtration, had an active oxygen content 2.07%. After two recrystallizations from pentane a material having mp 134–137° was obtained.

## The Thermal Decomposition of Organogermanium Peroxides and Hydroperoxides<sup>1</sup>

RALPH L. DANNLEY AND GEORGE C. FARRANT

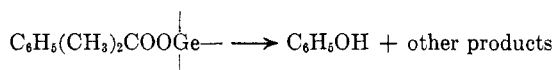
Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

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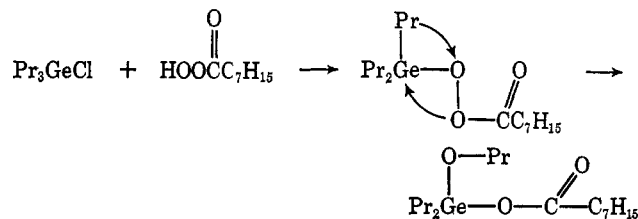
The thermal decomposition reactions of a number of organogermanium peroxides and hydroperoxides were studied to gain information about the mechanism of the cleavage of the peroxidic link when bound to germanium. Bis(triphenylgermyl) peroxide thermally decomposed with first-order kinetics ( $E_a = 33.7$  kcal/mol) in hexadecane in the absence of oxygen at 190–210° yielded phenol, diphenylgermanium oxide, triphenylgermanol, but no oxygen. The migratory aptitudes of the phenyl and the *p*-trifluoromethylphenyl groups in the decomposition of bis(diphenyl-*p*-trifluoromethylphenylgermyl) peroxide were about equal, consistent with a free-radical mechanism. The thermal decomposition of triphenylgermyl hydroperoxide (1.0 mmol) in *o*-dichlorobenzene produced oxygen (0.17 mmol), water (0.35 mmol), and triphenylgermanol (0.93 mmol) as the major products, and phenol (0.06 mmol) and diphenylgermanium oxide (0.07 mmol) as the minor products. The effect of solvents, radical initiators, radical inhibitors, and ultraviolet light were consistent with a radical mechanism producing these products. The products of the thermal decomposition of triphenylgermyl hydroperoxides in which one of the phenyl groups was substituted in the *para* position gave a migratory aptitude series (*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>, 1.98; *p*-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>, 1.36; C<sub>6</sub>H<sub>5</sub>, 1.00) consistent with a radical mechanism for the formation of phenols in this reaction. Triphenylgermyl hydroperoxide decomposed in *o*-dichlorobenzene at 150–170° in an initially oxygen-free system with zero-order kinetics at 0.01 *M* concentration ( $E_a = 35$  kcal/mol) but followed no simple order at higher concentrations. The thermal decomposition of tricyclohexylgermyl hydroperoxide (1.0 mmol) produced cyclohexene (0.56 mmol), cyclohexanol (0.06 mmol), tricyclohexylgermanol (0.29 mmol), and dicyclohexylgermanium oxide (0.18 mmol).

Although there have been several reports<sup>2–4</sup> of the synthesis of organogermanium peroxides, and a disclosure of the synthesis of organogermanium hydroperoxides,<sup>5,6</sup> relatively little is known about the stabilities of these substances or their decomposition products which would permit comparison with the analogous compounds of the other group IVb elements.

Davies<sup>4</sup> suggested a nucleophilic migration of the phenyl group to oxygen to explain his finding that 1-methyl-1-phenylethyl hydroperoxide and germanium tetrachloride gave rise in the course of a few days to phenol and other nonperoxidic products. However, the initial germanium peroxide was not isolated. Davies



also suggested a 1,2 rearrangement to explain his observation that the treatment of alkylgermanium chlorides with peroxy acids gave nonperoxidic products.<sup>4</sup>



(1) (a) Supported by the U.S. Army Research Office (Durham) through Grant No. DA-ARO(D)-31-124-G720. (b) Taken in part from the dissertation of G. C. Farrant submitted in Jan. 1968 to the Graduate School of Case Western Reserve University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (c) Presented in part at the first Central Regional Meeting of the American Chemical Society, Akron, Ohio, May 10, 1968.

Both Davies<sup>4</sup> and Rieche<sup>3</sup> and their coworkers postulated that germanium peroxides undergo some homolytic scission of the peroxide bond because the compounds catalyzed the polymerization of vinyl monomers. However, the extent of the radical *vs.* ionic processes in the decomposition of these compounds has not been established.

It was the purpose of the present investigation to determine whether the symmetrical peroxides and the hydroperoxides of germanium undergo homolysis or heterolysis of the peroxidic link and to determine the kinetics and products of the thermal decomposition.

### Results and Discussion

**Thermal Decomposition of Bis(triarylgermyl) Peroxides.**—The thermal decomposition of bis(triphenylgermyl) peroxide in hexadecane or *o*-dichlorobenzene occurs *via* a first-order process with an activation energy of  $33.7 \pm 1.5$  kcal/mol<sup>7</sup> (Table I). The products of

(2) A. Rieche and J. Dahlmann, *Angew. Chem.*, **71**, 169 (1959).

(3) A. Rieche and J. Dahlmann, *Ann.*, **675**, 19 (1964).

(4) A. G. Davies and C. D. Hall, *J. Chem. Soc.*, 3835 (1959).

(5) R. L. Dannley and G. Farrant, *J. Amer. Chem. Soc.*, **88**, 637 (1966).

(6) R. L. Dannley and G. Farrant, *J. Org. Chem.*, **34**, 2428 (1969).

(7) A referee has pointed out that the calculated value of  $\log A$  is ca. 12, which is considerably lower than the corresponding values of 15–16 [(a) R. Hiatt and K. C. Irwin, *J. Org. Chem.*, **33**, 1436 (1968)] for many carbon peroxide decomposition. However, peroxides of elements other than carbon do yield similar low values for their first-order thermal decompositions. Thus  $\log A$  is 10.1–10.8 for silicon hydroperoxides [(b) R. L. Dannley and G. Jalic, *ibid.*, **30**, 3848 (1965)], 11.4 for bisdiphenylphosphinic peroxide [(c) R. L. Dannley and K. R. Kabre, *J. Amer. Chem. Soc.*, **87**, 4805 (1965)], and 12.2 for trimethyltin hydroperoxide in dilute solution [(d) R. L. Dannley and W. A. Aue, *ibid.*, **30**, 3845 (1965)]. The mechanisms of all these reactions are not clearly established but they are first order with respect to peroxide and there is some evidence for free-radical intermediates.