

was 11 hours. The yield of crude product, light chocolate brown, was 32.7 g., or 89.5%.

Attempts to recrystallize this product from water or alcohol were not successful. It was purified, to some extent, by dissolving in very dilute hot sodium hydroxide solution, stirring with Nuchar, filtering and acidifying the filtrate. The material thus purified was lighter brown in color, m.p. 250–253° with decomposition. Its aqueous solution gave a faint reddish-brown color with ferric chloride solution.

Anal. Calcd. for $C_{13}H_{10}N_4O_2$: C, 61.4; H, 3.94; N, 22.05; atomic ratio C/N, 3.250:1. Found: C, 56.35; H, 3.99; N, 18.8; C/N, 3.40:1.

Decarboxylation of 5-Hydroxybenzotriazole-4-carboxylic Acid.—One gram of 5-hydroxybenzotriazole-4-carboxylic acid (melting at 200–202°) was dissolved in 140 ml. of water and refluxed for 20 hours. The solution was then evaporated to 8 ml., cooled to room temperature and filtered. The grayish-white crystalline precipitate was filtered, washed, and dried at 100°; yield 0.57 g., m.p. 234–234.5°; it did not depress the m.p. of pure 5-hydroxybenzotriazole (235–235.5°). A 0.1% aqueous solution of the product gave a very pale ferric chloride test, characteristic of 5-hydroxybenzotriazole and sharply distinguishable from the intense coloration given by a 0.1% solution of the 4-carboxylic acid.

Attempted Decarboxylation of 5-Hydroxybenzotriazole-6-carboxylic Acid.—One gram of 5-hydroxybenzotriazole-6-carboxylic acid was boiled in 140 ml. of water and filtered to remove a trace of insoluble residue. The filtrate was refluxed overnight, and then evaporated to about 6.5 ml., and cooled to about 5°. There was obtained 0.18 g. of light brown precipitate, consisting of minute short needles.

A few mg. of this material dissolved in 10 ml. of water gave a deep violet color with ferric chloride, showing that it was still the carboxylic acid. The m.p. was also unchanged.

Coupling Reactions. (1). **Preparation of 4-(*p*-Chlorophenylazo)-5-hydroxybenzotriazole.**—*p*-Chloroaniline (6.38 g., 0.05 mole) was dissolved in 100 ml. of 2.5 *N* hydrochloric acid and diazotized by the addition of 10 ml. of 5 *N* sodium nitrite solution at 10°. This solution was filtered and diluted to 200 ml. to make a 0.25 *M* solution. Eight ml. of

this diazo solution (0.002 mole) was added with stirring to a solution of 0.286 g. of 5-hydroxybenzotriazole (0.00212 mole) dissolved in a mixture of 40 ml. of water, 4 ml. of *N* sodium hydroxide and 2 ml. of *M* sodium carbonate solution. A deep orange solution was formed immediately. After 15 minutes stirring, the solution was acidified to congo red paper by the addition of 1 ml. of 5 *N* hydrochloric acid. The reddish-orange precipitate formed was filtered, washed and dried at 100°; yield 0.47 g., m.p. 247–248.5° (decomposes slightly above m.p.). This was recrystallized from chlorobenzene without raising the m.p.

Anal. Calcd. for $C_{12}H_8ClN_5O$: C, 52.6; H, 2.92; Cl, 13.0; N, 25.6. Found: C, 52.8; H, 3.00; Cl, 13.2; N, 25.7.

(2). **Coupling of Diazotized *p*-Chloroaniline with 5-Hydroxybenzotriazole-4-carboxylic Acid.**—A 500-ml., three-necked flask was equipped with mercury seal, stirrer, dropping funnel, air inlet tube extending to a point near the bottom of the flask and an upper air exit tube leading to a bubbling tube containing barium hydroxide solution. A solution of 1.88 g. of 5-hydroxybenzotriazole-4-carboxylic acid (0.0105 mole) in 55 ml. of *N* sodium hydroxide and 100 ml. of water was poured into the flask, and a stream of carbon dioxide-free air was bubbled through the flask and thence through the barium hydroxide solution in a test-tube. There was then added with stirring through the dropping funnel 50 ml. of 0.20 *M* *p*-chloroaniline diazo solution (0.01 mole). An orange-brown precipitate of dye was formed together with considerable foam. After a few minutes stirring, the mixture was acidified strongly to congo red paper by the addition, through the dropping funnel, of 20 ml. of 5 *N* hydrochloric acid (a few drops of octyl alcohol was used to abate the foam). A copious white precipitate of barium carbonate was immediately formed in the bubbling tube.

The dye was filtered, washed and dried; yield 2.55 g. Repeated recrystallization from chlorobenzene gave an orange microcrystalline dye, m.p. 235–245° (dec.), mixed m.p. with 4-(*p*-chlorophenylazo)-5-hydroxybenzotriazole, 235–245° (dec.).

BOUND BROOK, NEW JERSEY

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Tetraalkoxygermanes¹

BY OTTO H. JOHNSON AND H. E. FRITZ

RECEIVED JULY 25, 1952

The method of preparation, the yields and some of the common physical properties of six members of this series from tetramethoxygermane through tetrahexoxygermane and for tetracyclohexoxygermane are reported. Only one tetraalkoxygermane has been described previously.

Tetraethoxygermane was prepared by Tabern, Orndorff and Dennis² by the reaction between absolute ethanol and germanium tetrachloride in the presence of sodium metal. The melting point was reported as –81° and the boiling point as 185–187° at atmospheric pressure. Later Laubengayer and Brandt³ also prepared tetraethoxygermane and reported a boiling point of 187°. The same year Sidgwick and Laubengayer⁴ reported a density of 1.1278 at 30° for this compound.

The only other compound of this type reported in the literature is tetraphenoxygermane. This compound was prepared by Schwarz and Rein-

hardt⁵ by the reaction between germanium tetrachloride and sodium phenolate. It is described as distilling at 210–220° (0.3 mm.) as a colorless, viscous oil.

This paper is a recapitulation of the values of a number of physical constants of the the first seven tetraalkoxygermanes as determined in this Laboratory.

Experimental

A two-necked 500-ml. flask was fitted with a reflux condenser and a dropping funnel both equipped with drying tubes. In the flask was placed 200 ml. of the appropriate anhydrous alcohol to which 8.8 g. (0.38 mole) of metallic sodium was added. In the case of methanol and ethanol the sodium was added in one-half gram portions while with the higher alcohols it was added in one portion followed by heating. The time required for the formation of the sodium alkoxide varied from 15 minutes for methanol to three hours for *n*-pentanol.

(5) R. Schwarz and W. Reinhardt, *Ber.*, **65**, 1745 (1932).

(1) This investigation was supported entirely by a Grant-in-aid of Research from the Graduate School of the University of Minnesota. It is a pleasure to acknowledge their interest and assistance.

(2) D. L. Tabern, W. R. Orndorff and L. M. Dennis, *THIS JOURNAL*, **47**, 2043 (1925).

(3) A. W. Laubengayer and P. L. Brandt, *ibid.*, **54**, 550 (1932).

(4) N. V. Sidgwick and A. W. Laubengayer, *ibid.*, **54**, 950 (1932).

TABLE I
 ANALYTICAL DATA ON TETRAALKOXYGERMANES

Compound	Yield, %	Molecular wt.		Carbon, %		Hydrogen, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
Ge(OCH ₃) ₄	21	196.7	...	24.4	25.5	6.15	6.13
Ge(OC ₂ H ₅) ₄	65	252.8	256	38.0	38.7	7.97	8.14
Ge(OC ₃ H _{7-n}) ₄	57	308.9	319	46.6	47.1	9.13	9.39
Ge(OC ₄ H _{9-n}) ₄	74	365.1	369	52.6	52.9	10.02	9.89
Ge(OC ₅ H _{11-n}) ₄	55	421.2	421	57.0	57.3	10.52	10.40
Ge(OC ₆ H _{13-n}) ₄	56	477.3	451	60.4	60.2	10.97	11.02
Ge(OC ₆ H ₁₁) ₄ ^a	21	61.5	61.8	9.45	9.60

^a Tetracyclohexoxygermane.

When the reaction between the alcohol and the sodium was completed, 10 ml. (18.5 g., 0.0862 mole) of germanium tetrachloride was added dropwise over a period of about 10 minutes. The addition of the germanium tetrachloride caused an immediate exothermic reaction with the precipitation of white sodium chloride. After refluxing for 1.5 hours the sodium chloride was filtered off using a coarse sintered glass funnel and dried filter aid and the residue washed with 25 ml. of the appropriate anhydrous alcohol. In the case of the higher alcohols filtering is facilitated by keeping the solution hot.

The excess alcohol was then removed from the filtrate by distillation, using reduced pressure for the higher alcohols. The viscous, and in some instances waxy, residues were then distilled through a 10-cm. Vigreux column under reduced pressure. The separation by distillation is very good, the greatest deviation in the refractive index observed between the "crude" product and redistilled samples being ± 0.0005 .

Discussion

The percentage yields, molecular weight data and analytical data are given in Table I. Yields were reasonably high in each case with the exception of the tetracyclohexoxy compound. The determination of molecular weights was made by the freezing point method using benzene as a solvent.

The melting points and boiling points are given in Table II. Tabern, Orndorff and Dennis² reported a somewhat lower melting point of -81° for the tetraethoxy compound which is the only member of the series previously reported. The same investigators obtained a value of $185-187^\circ$ for the boiling point at atmospheric pressure.

 TABLE II
 MELTING POINTS AND BOILING POINTS OF TETRAALKOXYGERMANES

Compound	M.p., °C.	B.p., °C. (mm.)
Ge(OCH ₃) ₄	-18 ± 1	66-67 (36); 148-150 (722)
Ge(OC ₂ H ₅) ₄	-72 ± 1	71-72 (11); 188-190 (722)
Ge(OC ₃ H _{7-n}) ₄	Glassy solid at -170	108-109.5 (9); 238-239 (722)
Ge(OC ₄ H _{9-n}) ₄	Glassy solid at -170	140-148 (8); 286-288 (722)
Ge(OC ₅ H _{11-n}) ₄	Glassy solid at -170	120-123 (0.03); dec. ca 200 (722)
Ge(OC ₆ H _{13-n}) ₄	Glassy solid at -170	150-153 (0.04)
Ge(OC ₆ H ₁₁) ₄ ^a	Waxy solid ca. 65	166-167 (0.01)

^a Tetracyclohexoxygermane.

Table III reports the density, the refractive index and the heat of vaporization. The density

TABLE III

Compound	Density/25°	n_D^{25}	Heat of vap., cal./g. (calcd.)
Ge(OCH ₃) ₄	1.3247 ± 7	1.3968	52
Ge(OC ₂ H ₅) ₄	1.1288 ± 5	1.4052	44
Ge(OC ₃ H _{7-n}) ₄	1.0580 ± 7	1.4172	43
Ge(OC ₄ H _{9-n}) ₄	1.0173 ± 6	1.4255	39
Ge(OC ₅ H _{11-n}) ₄	0.9930 ± 2	1.4335	..
Ge(OC ₆ H _{13-n}) ₄	0.9682 ± 3	1.4372	..

was determined by means of a pipet type pycnometer the ends of which were fitted with ground glass caps. The determination of the density was made during a period of low relative humidity and hydrolysis was negligible. The refractive indices were determined on an Abbe refractometer.

The higher members of the series distilled with

 TABLE IV
 OBSERVED INFRARED FREQUENCIES OF THE ALKOXYGERMANES

Frequencies in cm.⁻¹; intensities as indicated: s, strong; m, medium; w, weak

Ge-(OCH ₃) ₄	Ge-(OC ₂ H ₅) ₄	Ge-(OC ₃ H ₇) ₄	Ge-(OC ₄ H ₉) ₄	Ge-(OC ₅ H ₁₁) ₄	Ge-(OC ₆ H ₁₃) ₄	Ge-(OC ₆ H ₁₁) ₄
2955 s	2930 s	2930 s	2920 s	2910 s	2895 s	2945 s
	2148 w					
2110 m	2092 w	2065 w	2040 w	2060 w	2055 w	
	1960 w	1950 w				
	1482 m					
1460 s	1443 s	1460 s	1464 s	1464 s	1464 s	1452 s
						1421 w
	1388 s	1388 s	1382 s	1384 s	1384 s	
						1373 m
			1340 w	1342 w	1342 w	
	1292 m	1301 w	1300 m	1297 w	1302 w	1289 m
		1280 w		1280 w		
1266 w		1261 m	1262 w		1266 w	1260 w
			1234 m	1242 w	1234 w	
				1213 m		
					1200 w	
1181 s		1180 m		1170 w		1189 w
	1163 s					
						1153 w
			1148 m	1146 w		
			1117 s	1117 m	1121 m	1128 m
	1095 s					
		1061 s	1068 s			
				1052 s	1056 s	
1040 s	1045 s	1044 s	1044 s			1047 s
			1029 s			
		1017 m			1019 s	1021 m
				1006 s		
			999 m			
		976 s		985 s		977 s
			966 s		966 w	
					936 s	
		927 w				
	908 s	908 w	903 w	907 s		
897 m						
		889 m			892 m	888 m
		866 m	869 s		871 w	865 m
						850 s
				842 w	840 m	
			832 w			
		808 w				
			814 w			
		795 m	795 w	799 m	795 w	797 m
				777 w		
					766 m	
			754 m			
						748 s
		727 m	721 m	735 s	726 s	
				699 s	687 s	670 s
	670 s	695 s	683 s	699 s		

some difficulty, the vapors showing a distinct reluctance to pass into the fractionating column. Heats of vaporization were calculated by the integrated form of the Clausius-Clapeyron equation

$$L = \frac{R(T_1 T_2)}{T_2 - T_1} \ln \frac{P_2}{P_1}$$

Infrared Data

The infrared spectra were observed in the Infrared Laboratory of the School of Chemistry under the direction of Dr. Bryce L. Crawford, Jr., using a Perkin-Elmer model 12C single-beam spectrometer. Spectra were recorded both for the pure liquid and for the dilute solution in carbon disulfide. Rocksalt and KBr prisms were used in the appropriate regions and a cell thickness of 0.025 mm. was used in all cases. The observed frequencies of the seven compounds are given in Table IV. The spectrum of tetramethoxygermane as a pure liquid using a KBr prism is given in Fig. 1; that of the pure

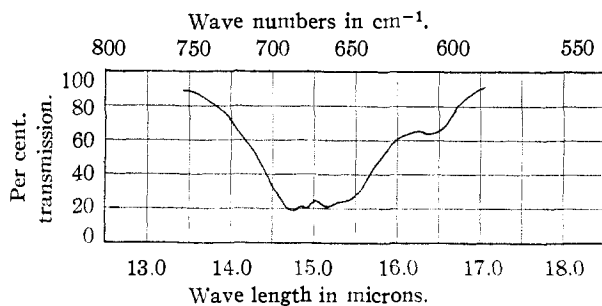


Fig. 1.—Infrared spectrum of tetramethoxygermane using a KBr prism.

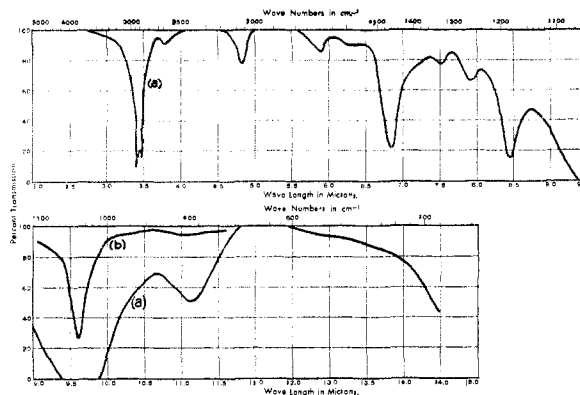


Fig. 2.—Curve (a), infrared spectrum of tetramethoxygermane using a NaCl prism; Curve (b), infrared spectrum of a 10% solution of tetramethoxygermane using a NaCl prism.

liquid using a NaCl prism in curve (a) Fig. 2 and that of the 10% carbon disulfide solution with a NaCl prism in curve (b) Fig. 2.

The strong absorption near 1040 cm^{-1} and the strong band near 680 cm^{-1} were observed with all these compounds and presumably arises from vibrations characteristic of the central GeO_4^{-4} configuration.

Extreme precautions had to be taken to avoid too much hydrolysis of the compounds while filling the cells. Occurrence of hydrolysis is readily detected through observation of the 3400 cm^{-1} OH band in the hydrolysis products.

MINNEAPOLIS 14, MINNESOTA

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, THE UNIVERSITY OF PENNSYLVANIA, AND THE LABORATORY OF CHEMICAL PHARMACOLOGY, NATIONAL CANCER INSTITUTE, NATIONAL INSTITUTES OF HEALTH]

The Synthesis of Deaminocolchicine Anhydride^{1,2}

BY JOHN KOO³

RECEIVED JULY 15, 1952

2,3,4-Trimethoxybenzosuber-5-ene-5,6-dicarboxylic anhydride (V), deaminocolchicine anhydride, has been synthesized. 2,3,4-Trimethoxybenzosuber-5-one (VI), an interesting intermediate for preparation of compounds related to colchicine, and some of the intermediates needed in the preparation of V and VI have been obtained by improved methods.

The complete syntheses of some methoxybenzosuberenedicarboxylic anhydrides^{4,5} with properties corresponding to that of Windaus' N-benzoylcolchicine anhydride⁶ have indicated the desirability of making a further study of 2,3,4-trimethoxybenzosuber-5-ene-5,6-dicarboxylic anhydride (V). This anhydride was then obtained by an essentially similar route and proved to be identical with the

deaminocolchicine anhydride,^{2,7} an important degradation product from natural colchicine.

It appears desirable to outline in some detail the experimental procedures employed in our synthesis of V, especially in view of the fact that the preparation by our method of some of the needed intermediates could not be reproduced readily by other workers⁸ in "the field." In addition, several compounds, such as 2,3,4-trimethoxybenzosuber-5-one^{8,9} (VI), an interesting intermediate for the preparation of compounds related to colchicine, have been prepared by greatly improved procedures in the course of this work.

(1) The work carried out in this paper was supported in part by a Grant-in-aid from the American Cancer Society recommended by the Committee on Growth of the National Research Council.

(2) Reported in part in a Communication to the Editor (E. C. Horning, M. G. Horning, J. Koo, M. S. Fish, J. A. Parker, G. N. Walker, R. M. Horowitz and G. E. Ulyot, *THIS JOURNAL*, **72**, 4840 (1950)).

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