completely negative test resulted. With Salkowski test, the chloroform was colorless and the sulfuric acid layer orange-yellow. With the Liebermann-Burchard test the color transitions were as follows: very slight pink, transitory lavender, deep blue, slowly to green.

α-Dihydro-ergosterol Benzoate.—The alcohol (0.1 g.) was dissolved in pyridine (2 cc.) and 2 drops of benzoyl chloride added. The benzoate precipitated and after long standing was filtered off and recrystallized from alcohol. It melted at 153–155°.

Anal. Calcd. for $C_{27}H_{43}OCOC_6H_5$: C, 83.55; H, 9.90. Found: C, 83.10; H, 10.33.

The benzoate gave the same color reactions described above and in addition gave a positive reaction to the Heilbron and Spring[8] modification of the Tortelli–Jaffe reaction.

Reduction to α-Ergostenol.—Three-tenths of a gram of the acetate was reduced with Adams' platinum oxide catalyst as previously described[9] and a top fraction of α-ergostenol acetate melting at 110–111° was obtained. Upon saponification with 3% methyl alcoholic potash, α-ergostenol melting at 133° was obtained.

Summary

From the unsaponifiable fraction of ergot fat, α-dihydro-ergosterol has been isolated. The alcohol itself melted at 172.5–175° and gave $[\alpha]_D^{26}$ $-20.6°$. The acetate of α-dihydro-ergosterol melted at 176–177° and the benzoate at 153–155°. The color reactions agree exactly with those described by Windaus and Brunken, and by Heilbron and Spring.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

STUDIES RELATING TO ORGANIC GERMANIUM DERIVATIVES. III. DIPHENYL GERMANIUM DIHALIDES AND DIPHENYL GERMANIUM IMINE

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I. Introduction

The present is one of a series of papers relating to the chemistry of the typical amphoteric elements. It may be considered that all the elements from the first to the seventh groups inclusive, which have a deficiency of from seven to one electrons with respect to the rare gas type, are amphoteric. The elements that have a deficiency of only one or two electrons are strongly electronegative and their amphoteric tendencies are not marked. On the other hand, those elements that have a deficiency of five, six or seven electrons usually act electropositively and their electronegative characteristics are not pronounced. Amphoteric properties are most marked in the elements of the fourth group, which have a deficiency of four electrons. In the case of carbon, this property is well illustrated by triphenylmethyl. The triphenylmethyl group combines, on the one hand, with negative

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[8] Heilbron and Spring, *Biochem. J.*, **24**, 133 (1930).

[9] Hart, Speer and Heyl, THIS JOURNAL, **52**, 2017 (1930).

elements or groups to form compounds that, under certain conditions, exhibit electrolytic properties. On the other hand, the same group combines with the alkali metals to form relatively stable compounds which are typical salts and in which the triphenylmethyl group acts as anion. Triphenylmethyl also exists in the neutral state. In other words, triphenylmethyl exists in three states of oxidation: as a positive group, as a neutral group, and as a negative ion.

While in certain respects carbon is the ideal amphoteric element, in other respects other elements of the fourth group exhibit amphoteric properties more commonly. Previous investigations have shown that the tertiary organic derivatives of tin, whether alkyl or aryl, are uniformly amphoteric.[1] And not only may we obtain univalent amphoteric groups in the case of tin; we may also obtain divalent groups. Thus Kraus and Greer[2] have shown that dimethyl tin acts electropositively toward the halogens, while it also combines with sodium to form a divalent anion. Similar properties have been found in the case of the diphenyl tin group.[1c]

Our knowledge of corresponding groups of germanium and silicon is very limited. In general, the study of these groups is rendered difficult because of the ease with which their halogen derivatives are ammonolyzed. Kraus and Foster,[3] however, have investigated the triphenyl germanium group. Investigations relating to silicon, germanium and boron have been under way in this Laboratory for some years and the results will be published from time to time. The present investigation is specifically directed toward the isolation of diphenyl germanium and the preparation and properties of some of its derivatives. It was found that the diphenyl germanium group lends itself to study less readily than do corresponding derivatives of tin. Furthermore, our knowledge of organic germanium derivatives generally is very limited so that it was found necessary to study many problems relating to source materials.

Among the earlier investigations relating to phenyl germanium derivatives may be mentioned those of Morgan and Drew,[4] who prepared tetraphenyl germanium and some other phenyl derivatives, and Tabern, Orndorff and Dennis,[5] who prepared tetraphenyl germanium as well as other quaternary alkyl and aryl germanium compounds. The work of Kraus and Foster, in this connection, has already been referred to.

In the present investigation, diphenyl germanium dihalides were first prepared and characterized. The action of ammonia and ethylamine on diphenyl germanium dihalides was also studied and, finally, diphenyl

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[1] (a) Kraus and Sessions, THIS JOURNAL, **47**, 2361 (1925); (b) Kraus and Bullard, *ibid.*, **48**, 2131 (1926); (c) Chambers and Scherer, *ibid.*, **48**, 1054 (1926).

[2] Kraus and Greer, *ibid.*, **47**, 2568 (1925).

[3] Kraus and Foster, *ibid.*, **49**, 457 (1927).

[4] Morgan and Drew, *J. Chem. Soc.*, **125**, 1261 (1924).

[5] Tabern, Orndorff and Dennis, THIS JOURNAL, **49**, 2512 (1927).

germanium was prepared in the free condition. Its physical properties and chemical reactions were investigated; disodium diphenyl germanide was prepared and octaphenyl germanopropane was synthesized. The two last-named compounds will be described in a succeeding paper.

II. Diphenyl Germanium Dihalides

Method of Preparation.—Tetraphenyl germanium served as source material for the preparation of the dihalides. This compound was prepared according to the method of Kraus and Foster[3] and preparative details need not be described here. It was recrystallized from trichloro-ethylene and melted at 230–231° (corr.).

According to Kraus and Foster, tetraphenyl germanium is brominated with considerable difficulty, although they were able to prepare the monobromide by boiling a mixture of the compound with the theoretical amount of bromine in carbon tetrachloride for a considerable period of time. The second phenyl group is substituted even less readily than the first. Preliminary experiments confirmed the observations of Kraus and Foster, but on further study it was found that the rate of bromination is greatly dependent upon the concentration of bromine. On boiling a mixture of 37 g. of tetraphenyl germanium and 15 cc. of bromine in 70 cc. of carbon tetrachloride for ten hours, a fairly satisfactory yield of diphenyl germanium dibromide was obtained. The product, however, was impure, containing some of the monobromide and a smaller proportion of the tribromide. Since completing the present investigation, Tabern, Orndorff and Dennis[5] have shown that tetraphenyl germanium is more readily brominated in ethylene dibromide.

In brominating tetraphenyl germanium, a mixture of bromides is in general obtained and separation becomes necessary. An attempt to fractionally distil the bromides did not prove particularly successful. Diphenyl germanium dibromide is not very volatile at 100°, even at a pressure as low as 0.005 mm. Accordingly, it was found more convenient to convert the mixture of bromides to chlorides. The original mixture was separated from residual impurities by vacuum distillation at 150°. The distillate was placed in an evaporating dish, a little alcohol was added and then strong ammonium hydroxide to complete the hydrolysis. The mixture was boiled for some time, in which process most of the phenyl bromide was carried off with the steam. On cooling, a mixture of oxides solidified. The solid mass was separated from the aqueous solution, washed and dried. These oxides were then converted to chlorides by heating with concentrated hydrochloric acid. The desired product settled to the bottom as a heavy liquid which was extracted with benzene. After removal of most of the solvent, the product was introduced into a special still and fractionated under reduced pressure.

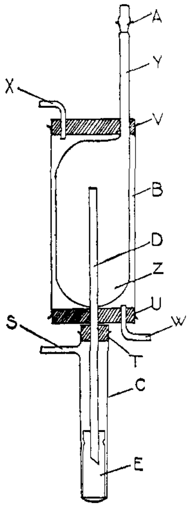

Fig. 1.

The distillation apparatus consisted of a pyrex tube Z, which was provided with a steam jacket B, the tubes X and W serving as inlet and outlet tubes, respectively. The liquid to be distilled was introduced through the tube Y, which was provided with a ground stopper A. The vapors from the liquid passed down through the re-entrant tube D. The condensate was collected in a small bottle E, which was contained in a wide test-tube C. This tube was attached to the distillation apparatus by means of a rubber stopper T. The side tube S, attached to the test-tube, was connected to a vacuum pump, a McLeod gage being connected in the exhaust line.

Diphenyl germanium dichloride distils readily at 100° under a pressure of 0.005 mm. The yield of dichloride, based on the weight of original tetraphenyl germanium used, ranged from 40 to 60%. The purity was tested by analysis.

Diphenyl Germanium Dichloride.—Diphenyl germanium dichloride is a colorless liquid. According to Sherman[6] it freezes at lower temperatures and melts at 9°. Its density is greater than that of water. It is readily soluble in ordinary organic solvents. It is slightly hydrolyzed in moist air, more rapidly in water and alcohol, and still more rapidly in alkaline solution.

The compound was analyzed for both germanium and chlorine. For the halogen determinations, from 0.2- to 0.3-g. samples were treated with dilute ammonium hydroxide, the mixture being stirred until the oxide was reduced to fine powder. It was then thrown onto a filter and the oxide was thoroughly washed. The ammoniacal filtrate was acidified with nitric acid and the chlorine was precipitated with silver nitrate and weighed as silver chloride.

Anal. Subs., 0.1836, 0.2460, 0.2721: AgCl, 0.1758, 0.2375, 0.2639. Calcd. for $(C_6H_5)_2GeCl_2$: Cl, 23.83. Found: Cl, 23.68, 23.88, 23.99; mean, 23.85.

The germanium was determined by a modification of the Krause method.[7] Samples of the dichloride were introduced into a pyrex tube (22 × 2.5 cm.) which had been heated to constant weight. About 5 cc. of fuming sulfuric acid was added with shaking, followed by 5 cc. of fuming nitric acid, which was added slowly. The mixture was then boiled for about twenty hours. Whenever the nitric acid content became low, as was indicated by the color of the fumes, more was added to the cooled solution. When oxidation was thought to be complete, the acids were boiled off. If the organic material was incompletely oxidized, a black deposit was formed on the walls of the tube as the residue dried up. In that case, more nitric acid was added and the sample was boiled for some hours longer. Removal of the acids was facilitated by drawing a gentle current of air through a glass tube, the end of which was located midway along the axis of the analysis tube. Certain of the phenyl germanium derivatives are oxidized with extreme difficulty. The method here described is effective in all cases provided that the process is continued for a sufficient length of time. After removing the acid, the oxide was ignited at a dull red heat until constant weight was reached.

Anal. Subs., 0.3068, 0.3161, 0.1940: GeO_2, 0.1085, 0.1115, 0.0677. Calcd. for $(C_6H_5)_2GeCl_2$: Ge, 24.39. Found: Ge, 24.54, 24.48, 24.22; mean, 24.40.

Diphenyl Germanium Dibromide.—Diphenyl germanium dichloride of known purity was hydrolyzed and the resulting oxide was converted to the dibromide by heating with strong hydrobromic acid. The oily liquid was extracted with benzene, the solvent was removed and the dibromide distilled in vacuo at 120° under a pressure of 0.007 mm. The properties of the dibromide correspond closely to those of the dichloride except that it is markedly less volatile.

The bromine content of the compound was determined by hydrolyzing a known sample of the compound with a weak solution of sodium hydroxide, separating the sodium bromide solution from the solid diphenyl germanium dibromide and precipitating the bromine as silver bromide. The germanium content was determined by the method already described in connection with the analysis of the dichloride.

Anal. Subs., 0.3542, 0.4068: AgBr, 0.3434, 0.3940. Calcd. for $(C_6H_5)_2GeBr_2$: Br, 41.35. Found: Br, 41.26, 41.22; mean, 41.24. Subs., 0.2275, 0.2117; GeO_2, 0.0620, 0.0572. Calcd.: Ge, 18.78. Found: Ge, 18.91, 18.75; mean, 18.83.

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[6] Unpublished observations by C. S. Sherman in this Laboratory.

[7] Krause, *Ber.*, **55**, 896 (1922); Kraus and Bullard, THIS JOURNAL, **51**, 3606 (1929).

Diphenyl Germanium Difluoride.—The difluoride was prepared by treating diphenyl germanium oxide (resulting from hydrolysis of the chloride) with hydrofluoric acid. Most of the excess acid was evaporated and the difluoride was extracted with benzene. After removal of the solvent, the fluoride was distilled *in vacuo* at 100° at a pressure of 0.007 mm. The germanium content of the difluoride was determined by the method already described.

Anal. Subs., 0.1490, 0.1471: GeO_2, 0.0585, 0.0576. Calcd. for $(C_6H_5)_2GeF_2$: Ge, 27.43. Found: Ge, 27.25, 27.18; mean, 27.22.

The fluorine was determined by the method of Starck.[8] The difluoride was hydrolyzed with sodium hydroxide and the solution separated from the resulting oxide by filtration. To the filtrate was added sixteen drops of concentrated hydrochloric acid, the solution being warmed to 40°. Methyl orange was then added and the solution acidified with nitric acid, allowing three drops in excess. Ten drops of glacial acetic acid and 25 cc. of a filtered solution (10%) of lead acetate containing 1% of acetic acid were added under stirring. Fluorine was precipitated as lead chlorofluoride. The precipitate was allowed to stand overnight, when it was filtered and weighed in a Gooch crucible.

Anal. Subs., 0.2983, 0.2944: PbClF, 0.5273, 0.5731. Calcd. for $(C_6H_5)_2GeF_2$: F, 14.36. Found: F, 13.93, 14.04; mean, 13.98.

Diphenyl germanium difluoride is a colorless liquid which is decidedly more volatile than the corresponding chloride. Of the three dihalides studied, it is the most sensitive toward moisture. On standing in the air but a short time, a film of oxide is formed on the surface of the liquid. This layer protects the remainder of the liquid against further hydrolysis. It is readily soluble in the common organic solvents.

III. Diphenyl Germanium Oxide

Morgan and Drew[4] have prepared diphenyl germanium oxide by hydrolyzing mixtures of bromides containing dibromide. From this mixture they separated a partially dehydrated hydroxide and a complex oxide that melted at 149 and 218°, respectively. It seemed worth while to examine the oxide obtained on hydrolyzing a pure dihalide. Accordingly, a quantity of the dichloride was hydrolyzed by the method already described. After drying, it was analyzed for germanium.

Anal. Subs., 0.1121, 0.1709: GeO_2, 0.0483, 0.0735. Calcd. for $(C_6H_5)_2GeO$: Ge, 29.92. Found: Ge, 29.90, 29.85; mean, 29.88.

Properties.—The oxide is a white powder which is practically insoluble in organic liquids. Of various samples tested, none was found to have a definite melting point. By extracting with boiling benzene, a minute quantity of oxide was obtained which melted between 133 and 150°. By means of boiling alcohol, small quantities were obtained that melted between 140 and 185° and 149 and 300°. The variation of the melting point indicates that, when the dihalides are hydrolyzed, a mixture of complex oxides is produced. It is doubtful whether the simple oxide $(C_6H_5)_2GeO$ can be obtained. A similar mixture of oxides is obtained by hydrolysis of diphenyl germanium imine.

IV. Action of Ammonia on Diphenyl Germanium Dichloride

Kraus and Wooster[9] have shown that triphenyl germanium halides are ammonolyzed by potassium amide in liquid ammonia. It was anticipated that the diphenyl germanium dihalides would be ammonolyzed by liquid ammonia. In preliminary ex-

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[8] Starck, *Z. anorg. Chem.*, **70**, 173 (1911); Hawley, *Ind. Eng. Chem.*, **18**, 573 (1926).

[9] Kraus and Wooster, THIS JOURNAL, **52**, 372 (1930).

periments, weighed samples of diphenyl germanium dichloride were sealed in fragile glass capsules which were introduced into one leg of a weighed two-legged reaction tube. This tube was provided with a stopcock through which it was evacuated prior to weighing, and through which ammonia could be introduced as desired. After evacuation, the bulb was broken, the tube was immersed in boiling ammonia and ammonia was condensed upon the dichloride. The reaction mixture was allowed to stand for several hours, after which the solvent was allowed to evaporate. The tube was then again exhausted and weighed. The increase in weight of the tube gave approximately the amount of ammonia added on ammonolysis. The results were as follows: wt. of $(C_6H_5)_2GeCl_2$, 0.2269, 0.2460, 0.2810; gain in wt. as NH_3, 0.0375, 0.0429, 0.0483; moles of NH_3 per mole of dichloride, 2.90, 3.05, 3.00; mean, 2.98. These data indicate that ammonolysis occurs according to the equation

$$(C_6H_5)_2GeCl_2 + 3NH_3 = (C_6H_5)_2GeNH + 2NH_4Cl \qquad (1)$$

In order to separate the organic material from the ammonium chloride, dry benzene was condensed on the product of reaction and the solution was decanted into the second leg of the reaction tube. By repeated distillation and decantation, complete separation of the ammonium chloride was effected. Most of the benzene was then removed by means of an aspirator pump and the last traces by means of a high vacuum pump. Dry nitrogen was introduced and the two legs were separated by sealing off the connecting tube with a blowpipe. The ammonium chloride left behind in the first leg of the reaction tube was analyzed for chlorine. The tube containing the salt was opened, the material was dissolved in water and the halogen determined as silver chloride in the usual way. The results follow, the percentages of chlorine being based on the weight of diphenyl germanium dichloride originally taken.

Anal. Subs., 0.2269, 0.2460, 0.2810: AgCl, 0.2202, 0.2375, 0.2371. Calcd. for $(C_6H_5)_2GeCl_2$: Cl, 23.83. Found: Cl, 24.00, 23.88, 24.04; mean, 23.94.

These results show that the ammonolysis of the dichloride was complete and in accord with Equation 1. Since the weight of the original products of the reaction indicated that three moles of ammonia were involved, the third molecule must have been combined with germanium as an imine group.

Diphenyl Germanium Imine.—The leg containing the soluble product of the reaction was evacuated and freshly distilled water was introduced. A white deposit gradually replaced the colorless viscous liquid in the tube. After standing for twenty-four hours, the stopcock of the tube was connected with a condenser and the liquid contents were distilled and collected in a flask. The distillate was titrated against standard acid.

Anal. $(C_6H_5)_2GeCl_2$, 0.2460, 0.2810: calcd. wt. of imine, 0.1998, 0.2282: cc. of 0.03043 *N* HCl used, 27.6, 30.7; N, 0.01176, 0.01309. Calcd. for $(C_6H_5)_2GeNH$: N, 5.80. Found: N, 5.89, 5.73; mean, 5.81.

The analyses show that one mole of ammonia is formed on hydrolysis of the imine. The white solid resulting on the hydrolysis of the imine was shown by analysis to be diphenyl germanium oxide.

Anal. Subs., 0.1709, 0.1121: GeO_2, 0.0735, 0.0483. Calcd. for $(C_6H_5)_2GeO$: Ge, 29.92. Found: Ge, 29.85, 29.90; mean, 29.88.

The imine is a colorless liquid which is extremely viscous at ordinary temperatures but becomes markedly more fluid at higher temperatures. It is readily soluble in ordinary organic solvents and is hydrolyzed with extreme ease.

Summary

Diphenyl germanium dibromide was prepared by the direct bromination of tetraphenyl germanium in boiling carbon tetrachloride. The mixture of

bromides so obtained was converted to oxides and in turn converted to the corresponding chlorides. The dichloride was obtained from this mixture by fractional distillation. Pure dibromide and difluoride were prepared by converting pure dichloride to its oxide and treating with hydrobromic or hydrofluoric acid.

The three dihalides are liquids at ordinary temperatures and are readily soluble in the common organic solvents. They may be distilled under pressures below 0.01 mm. at temperatures between 100 and 150°. The fluoride is markedly sensitive to moisture.

Diphenyl germanium imine was prepared by the action of liquid ammonia on diphenyl germanium dichloride. It is a highly viscous liquid at ordinary temperatures. It is readily soluble in the common organic solvents and is hydrolyzed with extreme ease.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, CASE SCHOOL OF APPLIED SCIENCE]

QUINAZOLINES. I. THE INTERACTION OF 2,4-DICHLOROQUINAZOLINE WITH SODIUM ALCOHOLATES AND SODIUM PHENATES WITH THE REPLACEMENT OF ONE HALOGEN TO FORM HALOGEN-OXYGEN ETHERS

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Since evodiamine and rutaecarpine, the alkaloids of *Evodia rutaecarpa*, have been shown to be derivatives of quinazolone[1] and since the quaternary salts of a few quinazolines have been found to have a lowering effect on the blood pressure,[2] it appears likely that other compounds of the quinazoline group might possess some desirable medicinal properties. It was during the course of a research now in progress in this Laboratory, the purpose of which was the preparation of a series of quinazoline derivatives for subsequent pharmacological testing,[3] that several anomalous compounds were obtained and a further investigation of these compounds was made because the quinazolines have an intrinsic interest of their own.

When 2,4-dichloroquinazoline (I) in alcohol is treated with sodium ethylate both halogens are replaced by ethoxy groups with the formation of 2,4-diethoxyquinazoline (V).[4] In attempting to prepare a similar ether of quinazoline with the phenolate of resorcinol in alcohol, several compounds were isolated from the reaction product which were found to differ from the expected ether. When phenol was substituted for resorcinol, it

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[1] Asahina, Manske and Robinson, *J. Chem. Soc.*, **129**, 1708 (1927).

[2] Gabriel and Colman, German Patent 161,401.

[3] The writers are indebted to Professor Marston Taylor Bogert for his suggestion that members of this group of compounds be prepared with this idea in mind.

[4] Abt, *J. prakt. Chem.*, [2] 39, 149 (1889).