6 or more moles of sodium hydroxylamine disulfonate which rapidly hydrolyzed to an acid solution of monosulfonate.

Preparation of Dimethylglyoxime.—The biacetyl monoxime and monosulfonate were filtered to remove any sediment, mixed in a 15-liter flask, the mixture was heated to 70° and allowed to remain warm and occasionally stirred for several hours. The dimethylglyoxime separated in crystals that were filtered from the solution after it had become cold. They were washed with cold water until free from sulfate; yield, 575 g.; 235–240°. Recrystallization was unnecessary since the product was pure white and free from tarry matter.

Summary

A study has been made of the conditions affecting the formation of dimethylglyoxime, and simplified and efficient methods have been devised for the preparation of biacetyl monoxime, sodium hydroxylamine monosulfonate and dimethylglyoxime.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM. XII. TETRA-ALKYL AND TETRA-ARYL COMPOUNDS OF GERMANIUM. GERMANIUM TETRA-ETHOXYL[1]

BY D. L. TABERN, W. R. ORNDORFF AND L. M. DENNIS

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The investigations of the organic compounds of silicon, begun by Friedel and Crafts in 1863, and continued during recent years by Kipping, Bygdén, Polis, Martin, Ladenburg and others, have shown that this element exhibits in this regard close similarity to carbon, its adjacent analog in Group IV.

Mendeléeff predicted in 1871 that ekasilicon (germanium), which follows silicon in Group IV of his Periodic Table, would form volatile "metallo-organic" compounds, such as tetra-ethyl.[2] That substance was prepared[3] in 1886 by Winkler, the discoverer of germanium, and it recently has been further studied by Dennis and Hance.[4] Morgan and Drew have described[5] a few substances of the type germanium-acetylacetone dichloride. These three articles are all that have hitherto appeared on the organic compounds of germanium.

In the systematic study of this class of substances which has now been taken up in the Cornell Laboratory, germanium tetrachloride was selected

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[1] The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] *Ann.*, 8th Spl., p. 202 (1871).

[3] Winkler, *J. prakt. Chem.*, **144** (N. F. 36), 177 (1887).

[4] Dennis and Hance, THIS JOURNAL, **47**, 370 (1925).

[5] Morgan and Drew, *J. Chem. Soc.*, **105**, 1261 (1924).

as the starting point since it can easily be prepared in high purity directly from germanium dioxide.

Preparation of Germanium Tetrachloride.—Germanium tetrachloride was made by Dennis and Hance[6] by passing chlorine over crystalline germanium at moderately elevated temperatures. This method necessitated the preparation of metallic germanium by reduction of germanium dioxide with hydrogen and the fusion of the product under salt. A simpler and shorter method which has since been devised consists in suspending germanium dioxide in concd. hydrochloric acid and passing hydrogen chloride into the warmed liquid. At about 70° germanium tetrachloride distils together with small amounts of hydrochloric acid. This distillate is placed in a distilling flask that carries a long inlet tube to which is attached a U-tube filled with calcium chloride, and the side arm of the flask is joined to a condenser. The receiver is connected to a water suction pump. The liquid in the flask is warmed until bubbles of hydrogen chloride freely escape. The flame is then removed and air is drawn through the apparatus. This procedure, repeated several times, removes nearly all of the free hydrogen chloride. The germanium tetrachloride is then distilled and the last traces of hydrogen chloride are removed from the distillate by adding to it solid sodium carbonate. The flask is allowed to stand overnight, and the sodium carbonate is then removed by filtration, the filtrate being received in a distilling flask and at once distilled again. The large middle fraction consists of very pure germanium tetrachloride.

The study of the behavior of germanium tetrachloride in the synthetic reactions of Grignard, Fittig and Friedel-Crafts was first taken up. The first two gave satisfactory results, but the Friedel-Crafts synthesis has thus far failed to yield the desired reaction.

Germanium Tetraphenyl, $Ge(C_6H_5)_4$

Synthesis by the Grignard Reaction.—Phenylmagnesium bromide was prepared with the use of 35 g. of bromobenzene, 4.8 g. of magnesium turnings and 100 cc. of dry ether. To this, 5.4 g. of germanium tetrachloride was added. The liquid was vigorously stirred during the energetic reaction that resulted, and was then refluxed for half an hour. Most of the ether was next removed by distillation, dry toluene was added and refluxing was carried on for two hours more during constant mechanical stirring. The material in the flask was then decomposed by pouring it into a dish containing ice and dil. acetic acid, the germanium tetraphenyl being held in solution by the addition of benzene. The layer of benzene was separated and filtered, and the greater part of the solvent was then removed by evaporation. The residue was converted to the crystalline form by treatment with ether. The product was next repeatedly crystallized from chloroform, the melting point of the successive preparations steadily rising until it reached 226°, at which it remained constant.

Synthesis by the Fittig Reaction.—Thirty-three g. of bromobenzene and 10.5 g. of germanium tetrachloride were dissolved in ether, and 10 g. of sodium wire was added

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[6] Dennis and Hance, This Journal, **44,** 304 (1922).

in small portions. Vigorous reaction soon began spontaneously and was controlled by external cooling. The product was refluxed for several hours, 100 cc. of benzene was then added and the ether was removed by distillation. The hot benzene was decanted from the residue of sodium chloride, which was then twice extracted with further amounts of hot benzene. The several portions of benzene were united, and the treatment above described, removal of the benzene and treatment with ether, yielded a white, crystalline product that melted at 225–226°.

The carbon and hydrogen in the two preparations were determined by combustion. In the determination of germanium, the sample was dissolved in fuming nitric acid in a platinum crucible. About 4 cc. of concd. sulfuric acid was added, the acids were then carefully fumed off and the residue was ignited and weighed as germanium dioxide.

Anal. (Fittig method) Subs., 0.1804, 0.2635: CO_2, 0.4995, 0.7304; H_2O, 0.0840, 0.1327. Subs., 0.1054: GeO_2, 0.0293. Calcd. for $GeC_{24}H_{20}$: C, 75.63; H, 5.31; Ge, 19.07. Found: C, 75.54, 75.62; H, 5.18, 5.61; Ge, 19.28.

(Grignard method) Subs., 0.1445: CO_2, 0.4011; H_2O, 0.0698. Subs., 0.1753: GeO_2, 0.0483. Found: C, 75.72; H, 5.37; Ge, 19.12.

Dr. C. W. Mason, Instructor in Chemical Microscopy in this Department, kindly examined the substance and reported as follows.

"Germanium Tetraphenyl.—Prisms and lath-shaped forms; few twins. Apparently tetragonal bipyramids of the first order and prisms of the second order. Terminal angles about 105°. Strong double refraction. Parallel extinction shown by all prismatic views. Optically negative. Highly refractive. In all probability isomorphous with the silicon tetraphenyl described by Polis."[7]

In this connection it may be of interest to record our use of the Fittig reaction in the preparation of tin tetraphenyl. Polis[8] states that the substance is not formed by the interaction of chlorobenzene, tin tetrachloride and sodium.

Using bromobenzene we succeeded, however, in preparing the tin tetraphenyl by the following procedure.

Thirteen g. of tin tetrachloride was slowly poured into cold ether which was actively stirred so as to produce the solid addition product in as finely divided form as possible. Twenty-three cc. of bromo-benzene was added and then 10 g. of sodium wire was introduced in small portions. Reaction took place at once and was carried to completion by refluxing the contents of the flask for ten hours. The ether was then removed by distillation and the residue of sodium halides was extracted thrice with boiling benzene which was finally filtered through a hot-water funnel. Upon evaporating the greater part of the benzene and adding ether, 10 g. of tin tetraphenyl separated. Its melting point, 223°, and its properties were in agreement with those given by Polis.

Germanium Tetra-*p*-tolyl, $Ge(C_6H_4.CH_3)_4$.—This substance was prepared by both the Fittig and the Grignard reactions, but the former gave the better yield.

Thirty-four and two-tenths g. of *p*-bromotoluene and 10.7 g. of germanium tetrachloride were dissolved in 300 cc. of dry ether, and 4.8 g. of sodium wire was gradually added. External cooling was employed to control the reaction and to lessen the formation of di-*p*-tolyl. After refluxing for half an hour, the solution was filtered through

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[7] Polis, *Ber.*, **19,** 1012 (1886).

[8] Polis, *Ber.*, **22,** 2915 (1889).

a hot-water funnel and the residue in the flask, consisting chiefly of sodium chloride and sodium bromide, was twice extracted with hot benzene which was also run through the filter. The solvents were removed by distillation, and the residual oily mass was subjected to prolonged steam distillation to remove toluene, unchanged *p*-bromotoluene and any di-*p*-tolyl that may have been formed. The pasty mass was then again dissolved in benzene, the solution was filtered, and most of the solvent was evaporated. Addition of ether yielded white, crystalline germanium tetra-tolyl. Repeated recrystallization from chloroform and benzene gave a pure product that melted at 224°. There also resulted from the reaction a considerable amount of a light-colored, viscous oil which could not be brought to crystallization.

Germanium tetratolyl is more soluble than the corresponding phenyl compound, and it decomposes to some extent when heated to its boiling point.

Anal. Subs., 0.1917, 0.1910: CO_2, 0.5407, 0.5399; H_2O, 0.1116, 0.1125. Subs., 0.1431, 0.2148: GeO_2, 0.0340, 0.0514. Calcd. for $GeC_{28}H_{28}$: C, 76.92; H, 6.46; Ge, 16.62. Found: C, 76.96, 77.11; H, 6.47, 6.56; Ge, 16.49, 16.61.

Dr. Mason's report on this compound was as follows.

"Rhomb-shaped tablets; acute angle of rhombs about 82.5°. Apparently, the monoclinic prism, basal pinacoid and + orthodome are present. Rather weak double refraction shown by tablets, since bisectrix is nearly perpendicular to them. Axial plane parallel to obtuse diagonal of rhombs; probably optically negative. Symmetrical extinction except for edge views which give oblique extinction. In all probability isomorphous with the corresponding silicon tetratolyl described by Polis."

Germanium Tetrapropyl, $Ge(C_3H_7)_4$.—Propylmagnesium bromide was prepared with the use of 50 g. of propyl bromide, 9.6 g. of magnesium and 200 cc. of ether.

After the reaction was complete the ether was removed by distillation and was replaced by dry benzene. Eleven g. of germanium tetrachloride, diluted with benzene, was slowly added, the contents of the flask being stirred and refluxed during the addition. Further boiling for one hour completed the separation of the magnesium halides. The product was decomposed by ice and acetic acid, the layer of organic solvents was separated and after drying was distilled. The fraction boiling from 200–230° was shaken with an equal volume of concd. sulfuric acid and was then washed with water, dried and distilled; b. p., 225° (746 mm.); yield, 76%.

Germanium tetrapropyl is a colorless, mobile liquid, whose odor somewhat resembles that of petroleum. It dissolves iodine, but does not appreciably react with it at 50°. It is ignited with difficulty and liberates a cloud of germanium dioxide when it burns; d^{20}_{20}, 0.9539; m. p., —73°; $n^{17.5}$, 1.451; n^{30}, 1.443; n^{45}, 1.440; n^{61}, 1.433.

Germanium in the compound was determined by dissolving the sample in ice-cold, fuming nitric acid and allowing the acid to act upon it overnight in a covered crucible. Concd. sulfuric acid was then added, the acids were fumed off and the residue was ignited at a red heat.

Anal. Subs., 0.1742, 0.1338: CO_2, 0.3771, 0.2880; H_2O, 0.1800, 0.1367. Subs., 0.1546, 0.1414: GeO_2, 0.0660, 0.0603. Calcd. for $GeC_{12}H_{28}$: C, 58.83; H, 11.52; Ge, 29.66. Found: C, 59.09, 58.73; H, 11.48, 11.35; Ge, 29.59, 29.62.

Germanium Tetra-*iso*amyl, $Ge(C_5H_{11})_4$.—Sixty-five g. of *iso*amyl bromide was gradually added to 9.6 g. of magnesium suspended in ether.

After the completion of the reaction, the ether was removed by distillation and was replaced by an equal volume of dry benzene. Eleven g. of germanium tetrachloride, diluted with benzene, was slowly added during stirring, and the mixture was boiled for three hours. The product was then decomposed in the usual manner and the solvents were removed by distillation. There remained in the flask a heavy oil which did not distil at atmospheric pressure without some decomposition. At 10mm. pressure it passed over almost completely at 163–164°; yield, 87%; d^{20}_{20}, 0.9147; $n^{17.5}$, 1.457; n^{30}, 1.451; n^{45}, 1.444; n^{61}, 1.438.

Anal. Subs., 0.2765, 0.3053: CO_2, 0.6837, 0.7507; H_2O, 0.3063, 0.3349. Subs., 0.2377, 0.2066: GeO_2, 0.0696, 0.0602. Calcd. for $GeC_{20}H_{44}$: C, 67.23; H, 12.42; Ge, 20.38. Found: C, 67.46, 67.08; H, 12.31, 12.19; Ge, 20.31; 20.22.

Germanium Tetra-ethoxyl, $Ge(OC_2H_5)_4$.—It was found that germanium tetrachloride did not react with boiling absolute alcohol. Reaction did take place, however, when 9.8 g. of sodium was dissolved in an excess of absolute ethyl alcohol and 20 g. of germanium tetrachloride was added slowly and during stirring.

The liquid was refluxed for several hours and was then cooled. The sodium chloride which had separated was removed by filtration and was washed with absolute ether. The solvents were removed by distillation and the residual liquid was distilled in a vacuum. A second distillation at atmospheric pressure yielded a fraction boiling at 185–187°.

Germanium tetra-ethoxyl is a colorless, mobile liquid which hydrolyzes readily in the air with the separation of germanium dioxide. The specific gravity and refractive index could not conveniently be determined because of the hygroscopic character of the compound; m. p., —81°.

Anal. Subs., 0.2658, 0.2143: CO_2, 0.3713, 0.2990; H_2O, 0.1441, 0.1162. Subs., 0.2288, 0.1944: GeO_2, 0.0947, 0.0804. Calcd. for $GeC_8H_{20}O_4$: C, 38.01; H, 6.02; Ge, 28.72. Found: C, 38.11, 38.07; H, 6.02, 6.02; Ge, 28.72, 28.70.

Germanium Tetra-ethyl.—Dennis and Hance prepared[4] this substance by the interaction of zinc diethyl and germanium tetrachloride. We have found that it can also be made by the Grignard reaction.

Forty-four g. of ethyl bromide and 9.6 g. of magnesium were converted into the Grignard reagent in the presence of 200 cc. of ether. To this was added 10.7 g. of germanium tetrachloride diluted with dry benzene. The liquid was boiled and stirred during the addition and was finally heated on a water-bath for three hours. The product was decomposed by ice and acetic acid, the layer of organic solvents was separated, and the ether and benzene were removed by distillation. The oily residue in the distillation flask was found to boil at 155–165°. It was treated twice with concd. sulfuric acid, and was then washed, dried and fractionally distilled. Almost all passed over between 162.5° and 163° (uncorr.); yield, 60%. Two separate preparations were combined, treated with iodine, distilled in steam first from hydrochloric acid and next from alkaline permanganate and then dried. The boiling point was the same as before. Determinations of the refractive index showed that the results obtained by Dennis and Hance were inaccurate, the errors having been found to be due to faults in the refractometer which was employed. For their values the following are to be substituted: $n^{17.5}$, 1.443; n^{30}, 1.439; n^{45}, 1.430; n^{61}, 1.422.

Summary

This article deals with the preparation of germanium tetrachloride directly from germanium dioxide, and with the preparation and some of the properties of germanium tetraphenyl, tetratolyl, tetrapropyl, tetra-*iso*-

amyl and tetra-ethoxyl. The synthesis of tin tetraphenyl by the Fittig reaction is also briefly described.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE BUREAU OF DAIRYING, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE NON-VOLATILE ORGANIC ACIDS OF ALFALFA

BY WILLIAM A. TURNER AND ARTHUR M. HARTMAN

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In view of the ready assimilation of calcium from green or well-cured alfalfa (*Medicago Saltiva*) by dairy cows, it is desirable to learn something of the state of combination of calcium in this important roughage. As a preliminary step in this investigation it was deemed advisable to determine the nature of the organic acids occurring in alfalfa.

Euler and Bolin[1] studying the oxidizing action of a substance obtained from the juice of alfalfa leaves, "medicago-laccase," identified mesoxalic, glycolic, malic and citric acids. They were interested primarily, however, in the enzyme and did not attempt a quantitative study of the acids of alfalfa. We have investigated only the non-volatile organic acids and those not completely. We hope to give a more complete report including the volatile acids in a later communication.

Green alfalfa plants (41.25 kg.) were chopped and twice ground in a meat grinder. The pulp thus obtained weighed 35.9 kg. Fourteen liters of 4.4% hydrochloric acid was added to insure the solution of calcium salts of organic acids. The mass was then pressed in a hand press, 25.55 liters of juice being obtained. Eight liters of water was added to the press cake and the mass was pressed again, 9.56 liters more of juice being obtained. The combined press juices (including added water and acid) were then concentrated in a steam-jacketed kettle to about 5 liters of dark, tarry liquid. To about half of this liquid 2 volumes of alcohol was added. A precipitate of protein was filtered off and discarded. The acidity of the filtrate was determined by titration with 0.5 N alkali, and sufficient lead acetate [$Pb(C_2H_3O_2)_2.3H_2O$] to react with all the acids present was added and the mixture filtered. The filtrate was very dark in color.

The precipitate, consisting of the lead salts of organic acids as well as lead sulfate, chloride and phosphate, was washed with hot water to remove a large part of the lead chloride. The precipitate of lead salts was then treated with slightly more than sufficient sulfuric acid to precipitate the lead as sulfate, which was discarded. The sulfuric acid in the filtrate was determined by precipitation with barium chloride, and an equivalent amount of barium hydroxide was added to neutralize it. The precipitate

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[1] Euler and Bolin, *Z. physiol. Chem.*, **41**, 1 (1909).