Pyridine-2,6-dialdoxime was obtained in colorless needles, m.p. 216° (from ethanol).

Anal. Calcd. for $C_7H_7N_3O_2$: C, 50.9; H, 4.2. Found: C, 50.9; H, 4.5.

Addition of an aqueous solution of iron(II) sulfate heptahydrate (0.59 g.) to a solution of this pyridine-2,6-dialdoxime (0.7 g.) in ethanol (10 ml.) caused development of an intense red color. Addition of sodium acetate solution caused a deep red solid to crystallize. It was recrystallized several times from hot water.

Anal. Calcd. for $C_{14}H_{11}N_6O_4FeNa$: C, 41.4; H, 2.7; Fe, 13.8; Found: C, 41.5; H, 3.2; Fe 13.1.

The equivalent conductivity at 23° was 124 ohms^{-1} indicating the salt to be a binary electrolyte.

2,6-Bis-(aminomethyl)-pyridine.—Glacial acetic acid (500 ml.) and zinc dust (400 g.) were added over a period of 2 hours to a stirred solution of pyridine-2,6-dialdoxime (25 g.) in ethanol (100 ml.). After standing overnight the solids were separated by filtration and well washed with ethanol and these washings added to the filtrate which was then evaporated almost to dryness *in vacuo*. A considerable excess of strong potassium hydroxide solution was then added and the oil which separated was taken up in ether (4 lots of 500 ml.). After removal of the ether the residual oil was distilled *in vacuo* and obtained colorless, b.p. 112° (1.2 mm.), (13 g., 63%). It solidified on standing but was difficult to handle because of its tendency to carbonate.

Anal. Calcd. for $C_7H_{11}N_3$: C, 61.3; H, 8.0; Found: C, 60.0; H, 7.9.

For analysis it was much better to prepare derivatives such as 2,6-bis-(piperonylideneaminomethyl)-pyridine colorless needles, from pyridine–ethyl acetate, m.p. 179°.

Anal. Calcd. for $C_{22}H_{19}N_3O_4$: C, 68.8; H, 4.8; Found: C, 68.7; H, 4.9.

2,6-Bis-(salicylideneaminomethyl)-pyridine, almost colorless needles (from ethanol), had m.p. 120°.

Anal. Calcd. for $C_{21}H_{19}H_3O_2$: C, 73.1; H, 5.5; Found: C, 72.9; H, 5.5.

Bis-[2,6-di-(aminomethyl)-pyridine] iron(II) Iodide.—The base XXVI (0.9 g.) was added to a solution of iron(II) sulfate heptahydrate (0.7 g.) in water (10 ml.). After filtration the resulting deep green solution was treated with saturated aqueous potassium iodide solution (5 ml.). The green complex iodide which separated was collected, washed and dried *in vacuo*. It did not melt below 300°.

Anal. Calcd. for $C_{14}H_{22}N_6FeI_2$; C, 28.8; H, 3.8; Fe, 9.6. Found: C, 28.6; H, 3.8; Fe, 9.6.

Allowing aqueous solutions of this salt to stand in air leads to decomposition and iron(III) hydroxide is deposited. The salt has a magnetic moment of 5.24 Bohr magnetons (23°).

Bis-(2,6-(diaminomethyl)-pyridine)-nickel(II) Bromide. (XXVI).—(0.6 g.) was added to a solution of nickel(II) sulfate sexahydrate (0.5 g.) in water (10 ml.). Addition of saturated aqueous potassium bromide solution (5 ml.) to the resulting deep mauve solution caused the complex nickel(II) bromide to separate. It crystallized from hot water in mauve needles which did not melt below 300°.

Anal. Calcd. for $C_{14}H_{22}N_6NiBr_2$: C, 34.1; H, 4.5; Ni, 12.0; Found: C, 33.8; H, 4.6; Ni, 11.7.

Condensation of Pyridine-2,6-dialdehyde with 1,6-Diaminohexane.—The following experiment was typical. A hot solution of pyridine-2,6-dialdehyde (3.5 g., 1 mole) in ethanol (20 ml.) was added to a hot solution of 1,6-diaminohexane (3 g., 1 mole) in ethanol (20 ml.) and the mixture boiled. Within 20 sec. a white solid had separated from the hot solution. It was collected and washed with hot ethanol. It was insoluble in most solvents but did dissolve on warming in dimethylformamide. However, this solution soon redeposited solid, probably because of molecular weight increase due to further condensation. The solid did not melt but decomposed when very strongly heated.

Anal. Calcd. for $(C_{13}H_{17}N_3)_n$: C, 72.6; H, 7.9; Found: C, 72.0; H, 7.9.

Addition of this dried, finely ground white polymer (0.65 g.) to a boiling solution of iron(II) sulfate heptahydrate (1.8 g., excess) in water (25 ml.) caused its transformation to a deep red powder. This was collected and well washed with water. It was insoluble in any of the common solvents.

Anal. Calcd. for $(C_{13}H_{17}N_3)_2\cdot FeSO_4\cdot 6H_2O$; C, 45.2; H, 6.7; Fe, 8.1. Found: C, 45.6; H, 6.5; Fe, 8.1.

This solid was found to be ferromagnetic with a molar susceptibility at 24° of 155,000 × 10^{-6} c.g.s. unit.

The finely ground polymer (0.5 g.) was suspended in ethanol (15 ml.) and a solution of cobalt(II) chloride sexahydrate in ethanol (50 ml.) added. The liquid was then gently refluxed. The white polymer gradually changed in color to deep brown but the solution was still a blue color after one hour. The solid polymer was again ground and reheated with the solution which eventually became colorless. The solid was then collected, well washed with ethanol and dried *in vacuo*.

Anal. Calcd. for $C_{13}H_{17}N_3CoCl_2$; C, 45.2; H, 5.0; Co, 14.2. Found: C, 44.9; H, 5.4; Co, 13.8.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY AT HARVARD UNIVERSITY]

Vinyl Derivatives of the Metals. IV. The Preparation of Vinylgermanium Compounds by the Grignard Method[1]

BY DIETMAR SEYFERTH

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The addition of germanium(IV) chloride to vinylmagnesium bromide in tetrahydrofuran solution results in moderate yields of hexavinyldigermane in addition to tetravinylgermane. Diethyldivinylgermane and ethyltrivinylgermane have also been prepared. Hexavinyldigermane is cleaved by bromine and by iodine to give trivinylgermanium bromide and iodide, respectively.

The use of the vinyl Grignard reagent in tetrahydrofuran solution for the preparation of vinyltin compounds[2] and vinylsilanes[3] has been reported recently. In the examples where tin(IV) chloride and tetrachlorosilane were vinylated only tetravinyltin and tetravinylsilane, respectively, were isolated.

We have now investigated the reaction of vinylmagnesium bromide[4] in tetrahydrofuran solution

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[1] Part III, D. Seyferth, *J. Org. Chem.*, **22**, in press (1957).

[2] D. Seyferth and F. G. A. Stone, THIS JOURNAL, **79**, 515 (1957).

[3] S. D. Rosenberg, *et al.*, Abstracts of Papers Presented at the 130th Meeting of the American Chemical Society, Atlantic City, September 1956, p. 81-O.

[4] H. Normant, *Compt. rend.*, **239**, 1510 (1954).

with germanium(IV) chloride and some ethylgermanium chlorides. Addition of germanium(IV) chloride to a slight excess of this Grignard reagent gave a 26% yield of hexavinyldigermane in addition to a 35% yield of the expected tetravinylgermane. Identification of the former compound was made on the basis of analysis, determination of molecular weight, molar refraction and its conversion to trivinylgermanium iodide by iodine cleavage and trivinylgermanium bromide by means of bromine cleavage

$$(CH_2{=}CH)_3GeGe(CH{=}CH_2)_3 + X_2 \longrightarrow 2(CH_2{=}CH)_3GeX$$

Johnson and Harris[5] have reported that hexaphenyldigermane is similarly obtained in the reaction of an excess of phenylmagnesium bromide with germanium(IV) chloride is an ether–toluene solvent system. No such reductive alkylation of germanium(IV) chloride has been observed with aliphatic Grignard reagents. Johnson and Harris made no attempt to explain their observed reaction, but it is noteworthy that they demonstrated that the phenylation of germanium(IV) chloride can be forced to give tetraphenylgermane exclusively by completely removing the ether and operating at the temperature of the refluxing toluene solution.

In the few years that have elapsed since the work of Johnson and Harris it has become increasingly apparent that the chemistry of germanium presents some anomalies, and that in some cases the reactions of certain germanium compounds do not parallel those of the corresponding silicon and tin compounds. For example, organogermanium halides can be reduced to the hydrides by zinc and hydrochloric acid[6]; this reaction is not observed with the corresponding chlorides of silicon and tin. Also, as Gilman and his co-workers have shown, the reaction of triphenylgermane with alkyllithium compounds results in the formation of triphenylgermyllithium,[7] while triphenylsilane[8] and triphenyltin hydride[9] are alkylated by alkyllithium compounds. These and other differences in the reactions of germanium compounds on one hand, and of silicon and tin compounds on the other, were explained by these and other workers[10] on the basis of a higher electronegativity of germanium, new experimental verification of which has now been provided in this Laboratory by Allred and Rochow.[11] It is interesting to note that such "reductive coupling" as described by Johnson and Harris and by the author of the present study has not been observed in the Grignard alkylation of tetrachlorosilane and tin(IV) chloride with phenylmagnesium and vinylmagnesium bromides, and it is possible that these results similarly could be a direct consequence of the high electronegativity of germanium, and that the reaction proceeds *via* an unstable or poorly stable intermediate containing a Ge–Mg bond. Work in this Laboratory[12] has shown that a germanium Grignard reagent of the type $(CH_3)_3GeMgCl$ does not form when trimethylgermanium chloride is treated with magnesium in diethyl or dibutyl ether in the presence or absence of a catalyst. Other workers[7] have shown that triphenylgermane does not exchange with a Grignard reagent. However, these observations do not preclude the possibility of an unstable $(CH_2{=}CH)_3GeMgBr$ or $(C_6H_5)_3GeMgBr$ intermediate in the "reductive coupling" reaction. Such an intermediate could possibly be formed in an exchange reaction between trivinylgermanium halide and vinylmagnesium bromide, but we consider it more likely that formation of such an intermediate would occur *via* primary reduction of $GeCl_4$ to $GeCl_2$ by the Grignard reagent, followed by vinylation to give divinylgermane(II). The latter could then add vinylmagnesium bromide

$$GeCl_4 + 2CH_2{=}CHMgBr \longrightarrow GeCl_2 + CH_2{=}CH{-}CH{=}CH_2 + MgCl_2 + MgBr_2$$

$$GeCl_2 + 2CH_2{=}CHMgBr \longrightarrow (CH_2{=}CH)_2Ge + MgCl_2 + MgBr_2$$

$$(CH_2{=}CH)_2Ge + CH_2{=}CHMgBr \longrightarrow (CH_2{=}CH)_3GeMgBr$$

$$(CH_2{=}CH)_3GeMgBr + (CH_2{=}CH)_3GeCl \longrightarrow (CH_2{=}CH)_3GeGe(CH{=}CH_2)_3 + {}^1/_2MgCl_2 + {}^1/_2MgBr_2$$

Both the reduction of metal halides to a lower oxidation state by Grignard reagents[13] and the addition of active organometallic reagents to diorganogermane(II) compounds[14] have been reported previously.

The vinylmonogermanes prepared in this study are much more stable with respect to cleavage reactions than are the corresponding vinyltin compounds.[1,15] Thus mercuric chloride in refluxing ether solution caused no cleavage of the vinylgermanium bond and no redistribution reaction was observed on refluxing a mixture of tetravinylgermane and germanium(IV) chloride. These indications that the Ge–C mean bond energy is considerably greater than that of the Sn–C bond in analogous organotin compounds are further borne out by the recently described successful side-chain chlorination of ethylgermanium trichloride.[16] Attempted side-chain chlorination of ethyltin trichloride resulted in Sn–C bond cleavage.[17] Hexavinyldigermane appears to be moderately stable in air, turning from colorless to light yellow in color over a period of several weeks.

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(5) O. H. Johnson and D. M. Harris, THIS JOURNAL, **72**, 5564 (1950); see also "Inorganic Syntheses," Vol. V, in press.

(6) R. West, *ibid.*, **75**, 6080 (1953).

(7) H. Gilman and C. Gerow, *ibid.*, **78**, 5435 (1956).

(8) H. Gilman and H. W. Melvin, *ibid.*, **71**, 4050 (1949).

(9) H. Gilman and S. D. Rosenberg, *ibid.*, **75**, 3592 (1953).

(10) R. T. Sanderson, *ibid.*, **74**, 4792 (1952).

(11) A. L. Allred, Ph.D. Thesis, Harvard University, 1956, found by means of nuclear magnetic resonance studies of tetravalent organic derivatives of the Group IV elements that the electronegativities of these elements are: C, 2.60; Si, 1.90; Ge, 2.00; Sn, 1.93; Pb, 2.45. A detailed report is soon to be published.

(12) A. L. Allred, private communication.

(13) See for instance: H. H. Zeiss and W. Herwig, THIS JOURNAL, **78**, 5959 (1956).

(14) (a) L. Summers, *Iowa State Coll. J. Sci.*, **26**, 292 (1952); (b) G. Jacobs, *Compt. rend.*, **238**, 1825 (1954).

(15) D. Seyferth, THIS JOURNAL, **79**, .2133 (1957).

(16) A. D. Petrov, *et al.*, *Izvest. Akad Nauk S.S.S.R., Otdel. Khim. Nauk*, 1146 (1956).

(17) C. R. Dillard, Final Report, U. S. Office of Naval Research Contract N9-onr-95700, August 31, 1952.

Experimental

1. **Diethyldivinylgermane.**—To 0.5 mole of vinylmagnesium bromide in 200 ml. of tetrahydrofuran[18] was added 18 g. (0.089 mole) of diethylgermanium dichloride, dissolved in an equal volume of tetrahydrofuran, at such a rate that a gentle reflux was maintained. The reaction mixture was refluxed for about 20 hours, then was cooled and hydrolyzed with 75 ml. of a saturated aqueous solution of ammonium chloride. The organic layer was decanted and the residual salts were washed with diethyl ether, the washings being added to the decanted liquid. Distillation of the solvents followed by fractional distillation of the residue gave 11.5 g. (70%) of diethyldivinylgermane, b.p. 59–60° at 28.5 mm., $n^{25}\text{D}$ 1.4540.

Anal. Calcd. for $C_8H_{16}Ge$: C, 51.99; H, 8.73. Found: C, 52.16; H, 8.80.

2. **Ethyltrivinylgermane.**—A similar procedure was followed in the reaction of 1.0 mole of vinylmagnesium bromide in 300 ml. of tetrahydrofuran with 35.3 g. (0.17 mole) of ethylgermanium trichloride. A 50% yield (15.5 g.) of ethyltrivinylgermane, b.p. 55–57° at 28 mm., $n^{25}\text{D}$ 1.4605, was obtained.

Anal. Calcd. for $C_8H_{14}Ge$: C, 52.56; H, 7.72. Found: C, 52.55; H, 7.62.

3. **Tetravinylgermane and Hexavinyldigermane.**—To a solution of 2.0 mole of vinylmagnesium bromide in 800 ml. of tetrahydrofuran was added 95.5 g. (0.445 mole) of germanium(IV) chloride at such a rate that a gentle reflux was maintained. The reaction mixture was then refluxed for about 20 hours. After it had cooled to room temperature the mixture was hydrolyzed with 300 ml. of a saturated aqueous solution of ammonium chloride. The orange organic layer was decanted and the residual salts were washed with ether, the washings being combined with the organic layer. After the solvents had been removed by distillation the brownish liquid residue was fractionally distilled to give: (a) **tetravinylgermane**, b.p. 52–54° at 27 mm., $n^{25}\text{D}$ 1.4676, $d^{25}{}_4$ 1.040; 28.5 g., a yield of 35.4%. *Anal.* Calcd. for $C_8H_{12}Ge$: C, 53.15; H, 6.69. Found: C, 53.00; H, 6.96; (b) a small middle run, boiling from 65° at 23 mm. to 89° at 4.2 mm., which turned grape red on standing in air; (c) **hexavinyldigermane**, b.p. 55° at 0.35 to 0.25 mm., $n^{25}\text{D}$ 1.5217, $d^{25}{}_4$ 1.171; 17.8 g., a yield of 26.1%. *Anal.* Calcd. for $C_{12}H_{18}Ge_2$: Ge, 47.23; C, 46.87; H, 5.90; mol. wt., 307.5. Found: Ge, 47.02; C, 47.00; H, 6.19; mol. wt. (Rast), 318.

The product from another run gave: C, 47.06; H, 6.14. The molar refractions calculated from the data did not check those calculated for any of the other possible higher boiling products such as $(Vi_3Ge)_2O$, Vi_3GeBr, Vi_3GeOH, Vi_2GeBr_2, Vi_2GeCl_2, $(Vi_2GeO)_n$ and others. No direct check was possible since the bond refraction of the Ge–Ge bond is not known. Using the refractive index and density listed above we calculate a value of 6.6 for the Ge–Ge bond refraction, which as expected, lies between the values of the Si–Si and Sn–Sn bond refractions.

4. **Trivinylgermanium Iodide.**—To a solution of 7.2 g. (0.023 mole) of hexavinyldigermane in 30 ml. of diethyl ether were added a few crystals of iodine. The iodine color was not discharged on refluxing the solution for one hour. When most of the ether had been replaced by chloroform the iodine was used up slowly on further heating. The rest of the iodine (5.94 g. total, 0.023 mole) was then added and the solution was refluxed for four hours. The solution at the end of this time was dark in color, but this did not appear to be due to free iodine. The chloroform was boiled off at atmospheric pressure and the dark residue was fractionally distilled to give 6 g. (45.6%) of trivinylgermanium iodide, b.p. 71–74° at 12 mm., and about 1 g. of unreacted digermane. Trivinylgermanium iodide is extremely sensitive to light; the initially colorless distillate rapidly turned reddish pink and darkened further on standing.

Anal. Calcd. for C_6H_9IGe: C, 25.68; H, 3.23; I, 45.22. Found: C, 26.20; H, 3.46; I, 44.84.

5. **Trivinylgermanium Bromide.**—To 10 g. (0.0325 mole) of hexavinyldigermane in chloroform solution was added dropwise a solution of 5.2 g. (0.0325 mole) of bromine in chloroform. The bromine was decolorized immediately in a very vigorous reaction and the solution soon began to reflux. After the addition was completed the solvent was boiled off and the residue was fractionally distilled to give 3.5 g. (23%) of trivinylgermanium bromide, b.p. 58° at 10 mm., $n^{25}\text{D}$ 1.5057.

Anal. Calcd. for C_6H_9BrGe: C, 30.84; H, 3.88; Br, 34.21. Found: C, 30.79; H, 3.99; Br, 34.23.

In addition, an unidentified high-boiling fraction distilled continuously from 75° at 6.0 mm. to 93° at 1.4 mm.

Trivinylgermanium bromide had the sharp smell and lachrymatory action normally associated with trialkyltin halides.

6. **Analyses** were performed by the Schwarzkopf Microanalytical Laboratories, Woodside 77, New York.

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[18] Tetrahydrofuran was obtained from the Electrochemicals Department, E. I. du Pont de Nemours & Co., and was purified by distillation from lithium aluminum hydride.