3,3-dimethyl-1-pentene, 4,4-dimethyl-2-pentene, 4,4-dimethyl-2-hexene and 2,2-dimethyl-3-hexene and their physical constants are recorded. These olefins are new.

As evidence that a skeletal rearrangement did not take place in the formation of these olefins, 4,4-dimethyl-2-pentene was hydrogenated to 2,2-dimethylpentane, 3,3-dimethyl-1-pentene to 3,3-dimethylpentane, 4,4-dimethyl-2-hexene to 3,3-dimethylhexane and 2,2-dimethyl-3-hexene to 2,2-dimethylhexane.

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Aliphatic Germanium Derivatives. III. Ethylgermanium Trihalides

BY E. A. FLOOD

Methods of preparation of ethylgermanium trihalides and some reactions of these compounds are described herein. In the preceding paper of this series it was pointed out that considerable difficulty is encountered in attempting to substitute a second bromine atom for an ethyl group in triethylgermanium bromide by the direct action of bromine.[1] It was therefore anticipated that the bromination of tetraethylgermane would not be a feasible method of obtaining monoethylgermanium derivatives. However, ethylgermanium triiodide can be obtained in almost quantitative yields from ethyl iodide and germanous iodide, which react according to the equation $C_2H_5I + GeI_2 = C_2H_5GeI_3$. Since germanium is readily extracted from its ore, germanite, as the volatile germanous sulfide which when treated with hydriodic acid yields GeI_2,[2] this method of preparing monoethylgermanium derivatives is simple and direct.

Ethylgermanium Triiodide, $C_2H_5GeI_3$.—When germanous iodide and an excess of ethyl iodide are heated together, in the absence of air, to a temperature of 110° reaction takes place over a period of several days with the formation of ethylgermanium triiodide, while if the reaction is carried out at a temperature of 140° a mixture of products is obtained, the chief constituents being germanium tetraiodide, unidentified gases and only very little ethylgermanium triiodide.

Preparation.—The following is a typical preparation of the triiodide from crude germanous iodide.

A mixture consisting of 18.5 g. of germanous iodide and 40 g. of ethyl iodide in an air-free sealed tube was heated to a temperature of 110° during three days. At the end of this period most of the solid had disappeared. The tube was opened and the liquid

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[1] E. A. Flood, THIS JOURNAL, **54**, 1663 (1932).

[2] Johnson, Morey and Kott, *ibid.*, **54**, 4278 (1932).

transferred to a vacuum fractionating apparatus in which the excess ethyl iodide was separated from the reaction product and the residual liquid product subjected to several fractional distillations *in vacuo*. Traces of iodine were removed from the impure triiodide during the second distillation by means of finely divided silver which had been previously placed in the apparatus. A small quantity of germanium tetraiodide and 23.5 g. of a high boiling yellow colored liquid were finally obtained. The liquid product was analyzed for iodine and germanium and thus shown to be ethylgermanium triiodide.

Anal. Calcd. for $C_2H_5GeI_3$: I, 78.93; Ge, 15.05. Found: I, 78.97, 79.02. Ge, 15.11, 15.16.

The yield of 23.5 g. of the triiodide corresponds to 86% of the germanous iodide. Since the germanous iodide was known to be somewhat impure due to exposure to air the yield was considered satisfactory.

Properties.—Ethylgermanium triiodide is a mobile lemon-yellow colored liquid. The color, however, deepens as the material is heated, becoming deep red at temperatures about 250°. The triiodide boils at a temperature of 281° under a pressure of 755 mm. while the melting point is between -1.5 and -2.5°. The triiodide dissolves in ordinary organic solvents without apparent change. It is ammonolyzed completely when treated with liquid ammonia, yielding an insoluble white solid, while when treated with water the triiodide dissolves with partial hydrolysis. Ethylgermanium triiodide is relatively stable toward thermal decomposition and may be heated to a temperature of 300° without appreciable change. In this respect its behavior is in marked contrast to that of germano-iodoform which is reported to decompose at room temperature, yielding germanous iodide and hydrogen iodide.[3] Attempts to decompose ethylgermanium triiodide analogously failed. When heated above 350° decomposition takes place with the formation of gas and germanium tetraiodide. While the triiodide does not react appreciably with "molecular" silver at temperatures as high as 220°, it reacts slowly with hot mercury and rapidly with other more electropositive metals at temperatures as low as 100°. Ethylgermanium triiodide is somewhat more stable toward oxidation than might be expected and may be distilled in dry air without change; however, when exposed to air containing traces of moisture marked decomposition occurs.

Monoethylgermanic Oxide $(C_2H_5GeO)_2O$.—When an aqueous solution of ethylgermanium triiodide is boiled with freshly prepared silver oxide, the hot solution filtered and the filtrate concentrated by evaporation, a transparent "cellophane-like" material forms on the surface of the hot solution. On removal of this material from the surface, the surface is soon covered with another solid film. A sample of this "glassy" material which had been dried in an air-bath at a temperature of 110° for one to two hours was shown by analysis to be monoethylgermanic oxide, $(C_2H_5GeO)_2O$.

Anal. Calcd. for $(C_2H_5GeO)_2O$: Ge, 57.78; C, 19.10; H, 4.01. Found: Ge, 57.83, 57.89, 57.82; C, 19.13, 18.99; H, 4.00, 3.93.

The residue obtained by evaporation of the remainder of the solution from which the sample of solid film was obtained, was also found to be monoethylgermanic oxide. Although this method of obtaining the ethylgermanic oxide is conveniently simple, the yields of the germanium compound were always low. Usually not more than 50% of the germanium was obtained as monoethylgermanic oxide.

A more satisfactory method of obtaining ethylgermanic oxide consists in ammonolyzing ethylgermanium triiodide with liquid ammonia, washing the insoluble white ammonolytic product, first with liquid ammonia and finally with cold water. When the washings are found to be iodide-free, the residual solid is dissolved in boiling water, the solution filtered and evaporated. The yields obtained by this method were usually

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(3) Dennis and Judy, THIS JOURNAL, **51**, 2326 (1929).

almost quantitative. Of course prolonged washing of the ammonolytic product with water dissolves some of the material, thereby lowering the yield.

Vapor pressure measurements carried out in an attempt to detect a hydrated form of $(C_2H_5GeO)_2O$ failed and indicated that the composition of the solid separating from the saturated solution of the oxide at room temperature has an empirical formula corresponding to $(C_2H_5GeO)_2O$.

Properties.—Monoethylgermanic oxide is a white solid which does not melt when heated to a temperature of 300° but when heated to higher temperatures *in vacuo* sublimation and decomposition occur. The oxide is soluble in water and alcohol and insoluble in petroleum ether. When treated with concentrated solutions of the halogen acids the corresponding trihalide is formed in solution and in the case of the trichloride may be extracted with ether.

Ammonolysis of Ethylgermanium Triiodide.—When liquid ammonia was condensed onto ethylgermanium triiodide contained in a suitable reaction tube, reaction occurred immediately yielding a white precipitate insoluble in liquid ammonia. On the addition of sodium to the mixture hydrogen was at once evolved. When an excess of sodium had been added the hydrogen collected was equivalent to the iodine of the triiodide, showing that the iodide was ammonolyzed. The sodium reacted only with the ammonium iodide formed and not with the ammonolytic germanium product. In order to determine the nature of the germanium compound formed in the reaction, the number of moles of ammonia entering into reaction with one mole of ethylgermanium triiodide was determined. The procedure consisted in condensing liquid ammonia onto a weighed sample of triiodide in a suitable reaction tube of known weight, agitating the mixture thoroughly, removing the excess ammonia by means of a vacuum pump, and reweighing the reaction tube. From the gain in weight of the reaction tube the number of moles of ammonia entering into reaction with the triiodide is at once obtained. In some cases the reaction tube was exhausted to about 0.01 mm. at −33° as quickly as possible, while in others the tube was evacuated at room temperatures during many hours. In all cases the gain in weight of the reaction tube corresponded to about 4.17 moles of ammonia per mole of the triiodide. However, when the reaction product in the closed tube was heated to a temperature of 150° during half an hour ammonia was evolved. The tube and its contents were cooled to room temperature, the tube opened and the liberated ammonia removed by means of a vacuum pump. The weight of the reaction tube after heating indicated that four moles of ammonia had entered into reaction with the triiodide. The over-all reaction is thus $C_2H_5GeI_3 + 4NH_3 = C_2H_5GeN + 3NH_4I$, while either a complex intermediate reaction or an unusual adsorption phenomenon occurs. As a check on these results water was condensed into the reaction tube and the mixture allowed to stand for several hours. Finally, the excess water as well as the ammonia liberated by hydrolysis of the nitride was removed from the reaction mixture by means

TABLE I

AMMONOLYSIS OF ETHYLGERMANIUM TRIIODIDE

	$C_2H_5GeI_3$,	NH_3[1], g.		Mole NH_3[a] mole $C_2H_5GeI_3$		H_2O-NH_3[b]	
Expt.	g.	a	b	a	b	Calcd.	Obs.
1	1.3374	0.1972	...	4.177	...	...	...
2	0.4541	.0667	...	4.161	...	...	...
3	1.1327	.1665	0.1599	4.164	3.999	0.0235	0.0250
4	1.0740	.1576	.1511	4.170	3.999	.0222	.0231

[a] The weight of NH_3 in column a is the weight of ammonia before heating the tube, while in column b the weights are those obtained after the heating process. The mole ratios are based on these weights.

[b] The values are calculated from equation 3 and the original weight of sample.

of a vacuum pump and the reaction tube reweighed. The results of these experiments were consistent with the previous observations and indicated that the nitride hydrolyzed as anticipated, according to the equation $2C_2H_5GeN + 3H_2O = (C_2H_5GeO)_2O + 2NH_3$. The results are recorded in the table.

The ammonolysis of ethylgermanium tribromide was also studied and confirmed the above results, four moles of ammonia per mole of tribromide being obtained for the over-all reaction, while for the intermediate reaction an average of 4.17 was found.

Ethylgermanium Tribromide, Trichloride and Trifluoride.—The three halides were prepared by passing the dry hydrogen halide over a mixture of phosphorus pentoxide and ethylgermanic oxide. The liquid products were purified by fractional distillation *in vacuo* and the pure trihalide kept in sealed fragile bulbs. The tribromide was analyzed for germanium and bromine, and the trichloride for chlorine, while the trifluoride was identified by vapor density determinations together with a semi-quantitative determination of the fluorine content wherein the fluorine was weighed as lead chlorofluoride.

Anal. Calcd. for $C_2H_5GeBr_3$: Br, 70.23; Ge, 21.27. Found: Br, 70.18, 70.20; Ge, 21.38, 21.58. Calcd. for $C_2H_5GeCl_3$: Cl, 51.14. Found: Cl, 50.96, 50.89. Calcd. for $C_2H_5GeF_3$: F, 35.9; mol. wt., 158.5. Found: F, 36.5; mol. wt. (vap. density), 159.5.

Properties of Ethylgermanium Trihalide.—These three halides are colorless mobile liquids which fume in air. The boiling points of the tribromide, trichloride and trifluoride are, respectively, 200° (763 mm.), 144° (762 mm.), and 112° (750 mm.). Ethylgermanium trifluoride melts between −15.5 and −16.5° while neither the tribromide nor the trichloride freeze when cooled in a bath of liquid ammonia boiling at atmospheric pressure. Like the triiodide the hydrolysis of these halides is homogeneous, and they are ammonolyzed when treated with liquid ammonia and soluble in common organic solvents.

Summary

Ethylgermanium triiodide was prepared by the action of ethyl iodide on germanous iodide. From the ammonolysis of ethylgermanium triiodide monoethylgermanium nitride was obtained. Hydrolysis of the nitride gave monoethylgermanic oxide. From the reaction of monoethylgermanium oxide and halogen halides, ethylgermanium trihalides were prepared.

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