made up by weight in *n*-heptane which had been cleaned so as to transmit in our 0.013-cm. cells to 1700 Å.[9]

**Acknowledgment.**—We are indebted to Prof. Weldon G. Brown for supplying the compounds and to Prof. R. S. Mulliken and to C. C. J. Roothaan for helpful discussions on the interpretation of the spectra. Mrs. Dorothy Iker Lossy assisted ably in photometering the plates and reducing the data.

### Summary

1. The effects of steric inhibition of resonance on the absorption spectra of substituted dimethylanilines to 1700 Å. have been determined.

2. Total oscillator strengths have been shown to decrease almost linearly with the van der Waals radius of the group substituted in the ortho position,

3. The minimum angle of twist of the $-N(CH_3)_2$ group with respect to the ring was estimated from the van der Waals radius of each crowding group. Within the accuracy of the estimates, the oscillator strengths of the different bands vary with the cosine-square of the angle.

4. With certain simple assumptions, purely spectroscopic calculations were made of the angle of twist and of the variation of the $N-C_6H_5$ bond order and bond distance, These predictions could be tested by electron or X-ray diffraction.

5. The three strong aniline bands transform into the three alkylbenzene bands with respect to both intensity and position as the angle of twist approaches 90°.

6. A plot of log oscillator strength of the 2500 Å. bands in mono-substituted benzenes *versus* ionization potential of the substituents shows a straight line relationship when the connecting atoms are in the second row of the periodic table and have small double-bond character. Aniline lies on this curve, which goes from toluene at one extreme to diphenyl at the other.

7. The conclusion from (5) and (6) is that the bands of all these compounds are derived from the parent benzene bands with very little change of position and with regular changes of intensity according to rule (6).

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

# The Preparation and Properties of Some Substituted Germanes[1]

BY O. H. JOHNSON AND W. H. NEBERGALL

## I. Preparation of Substituted Germanes by Alkyl- or Aryllithium Compounds

In an earlier paper[2] it was reported that attempts to prepare isopropyltricyclohexylgermane, phenyltricyclohexylgermane and tetracyclohexylgermane by treatment of bromotricyclohexylgermane with the appropriate Grignard reagent were unsuccessful, although the reaction between bromotricyclohexylgermane and methyl-, ethyl-, *n*-propyl-, *n*-butyl-, *n*-amyl- and benzylmagnesium bromides proceeded readily. In the present investigation the organolithium compounds, isopropyllithium, phenyllithium and *o*-tolyllithium were employed in the reaction

$$(C_6H_{11})_3GeBr + RLi \longrightarrow (C_6H_{11})_3GeR + LiBr$$

to determine whether or not the use of these more vigorous alkylating and arylating agents would result in the formation of the substituted tricyclohexylgermanes which were not produced by the use of Grignard reagents.

The preparation of phenyltricyclohexylgermane was successful, but it was found that neither the isopropyl nor the *o*-tolyl groups could be substituted for the bromine by the action of isopropyllithium and *o*-tolyllithium, respectively, upon bromotricyclohexylgermane. In addition, the reaction of cyclohexyllithium in large excess with germanium tetrachloride resulted in the formation of chlorotricyclohexylgermane[3] as the sole product.

$$GeCl_4 + 3C_6H_{11}Li \longrightarrow (C_6H_{11})_3GeCl + 3LiCl$$

Likewise, an excess of cyclohexylmagnesium bromide reacted with tetraethoxygermane to form bromotricyclohexylgermane.

Application of the organolithium technique in the preparation of tetrasubstituted germanes gave decidedly better yields than the standard Grignard and Fittig procedures. For example, Simmons, Wagner and Muller[4] reported poor yields in the synthesis of tetraarylgermanes by the classical methods of Grignard and Fittig although Worrall[5] obtained an 80% yield of tetraphenylgermane by the usual Grignard technique by substituting toluene for ether as the solvent. The writers obtained a 90% yield of tetraphenylgermane by the reaction of an excess of phenyllithium with germanium tetrachloride in ether solution.

## II. Action of Lithium Aluminum Hydride upon Some Substituted Germanes

The interaction of lithium aluminum hydride with the appropriate halides of silicon, of germa-

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(1) From a thesis submitted by William H. Nebergall to the Graduate School of the University of Minnesota in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

(2) Johnson and Nebergall, THIS JOURNAL, 70, 1706 (1948).

(3) The description of the preparation of chlorotricyclohexylsilane by a similar procedure will appear in a later paper.

(4) Simmons, Wagner and Muller, *ibid.*, 55, 3705 (1933).

(5) Worrall, *ibid.*, 62, 3267 (1940).

nium and of tin in the presence of ethers to give the corresponding hydrides has been reported recently by Finholt, *et al.*[6] The authors have applied this technique to the reduction of chlorotricyclohexyl- and bromotriphenylgermane according to the equation

$$4R_3GeX + LiAlH_4 \longrightarrow 4R_3GeH + LiX + AlX_3$$

Nystrom and Brown[7] report that alcohols represent the final stage of the reduction of the carbonyl group by lithium aluminum hydride. The writers have found that tricyclohexylgermanol, a germanium analog of a tertiary alcohol, is readily reduced to tricyclohexylgermane by this reagent for which reaction the following equation is proposed

$$4(C_6H_{11})_3GeOH + LiAlH_4 \longrightarrow 4(C_6H_{11})_3GeH + LiOH + Al(OH)_3$$

In addition, di-triphenylgermyl oxide, $[(C_6H_5)_3Ge]_2O$, has been reduced to triphenylgermane by lithium aluminum hydride.[8]

## III. Some Reactions of Tricyclohexylgermane and Tricyclohexylgermanol

The germanium–hydrogen linkage of tricyclohexylgermane is apparently quite weak in light of the fact that this germane is readily oxidized to the corresponding germanol on standing in the air for a short time. The corresponding phenyl compound, triphenylgermane, was found to be somewhat more stable in air and indications of oxidation became apparent only upon long standing, an observation which is in agreement with that of Kraus and Foster.[9]

Tricyclohexylgermane reacts immediately with the halogens to form the tricyclohexylgermyl halides.

Tricyclohexylgermanol was found to react with acetyl chloride to form chlorotricyclohexylgermane and with acetic anhydride to yield acetoxytricyclohexylgermane, $(C_6H_{11})_3GeOCOCH_3$.

## Experimental

**Reaction of Cyclohexyllithium with Germanium Tetrachloride.**—Cyclohexyllithium was prepared by adding over a period of four hours 95 g. (0.8 mole) of chlorocyclohexane to 500 ml. of low-boiling petroleum ether containing an excess of lithium metal shot[10] in a one-liter, three-necked flask fitted with a mercury-sealed, air-driven stirrer, a reflux condenser protected by a calcium chloride tube, and a dropping funnel containing the chlorocyclohexane. The reaction mixture was stirred and heated on a warm water-bath to initiate the reaction, after which the heat of reaction caused continuous refluxing for two hours after all of the chlorocyclohexane had been added. Without filtering out the lithium chloride and excess lithium, 21.4 g. (0.1 mole) of germanium tetrachloride[11] in 50 ml. of petroleum ether was added dropwise to the reaction mixture which was stirred and cooled in an ice-water-bath during the entire addition. The mixture was held at the reflux temperature for sixteen hours, the lithium chloride and excess lithium were then filtered out and the excess cyclohexyllithium was destroyed with dilute hydrochloric acid while the reaction mixture was stirred and cooled in an ice-water-bath. Then the organic layer was separated, dried over anhydrous calcium chloride, and the solvent was removed by distillation leaving an oily residue. The product, which was crystallized from glacial acetic acid and recrystallized from low-boiling petroleum ether, proved to be chlorotricyclohexylgermane, $(C_6H_{11})_3GeCl$; m. p. 101°[12]; yield 25 g. (70%).

*Anal.*[2] Calcd.: C, 60.49; H, 9.31; Ge, 20.3. Found: C, 60.32; H, 9.48; Ge, 20.5.

**Reaction of Tetraethoxygermane and Cyclohexylmagnesium Bromide.**—Preparation of tetraethoxygermane: To 150 ml. of absolute ethanol in a flask arranged to exclude moisture was added 9.2 g. (0.4 mole) of sodium. When the reaction with sodium was practically complete, the mixture was cooled and stirred while 20 g. (0.093 mole) of germanium tetrachloride was carefully added by means of the separatory funnel.. The mixture was then refluxed for 24 hours and filtered on a Buchner funnel. Filtration of the finely divided sodium chloride was facilitated by use of fine textured filter paper covered with a pad of glass wool. The filtrate was then fractionated by distillation under reduced pressure.

An anhydrous ethyl ether solution of 5.1 g. (0.02 mole) of tetraethoxygermane was added to a cold ether solution of cyclohexylmagnesium bromide made from 32.6 g. (0.2 mole) of bromocyclohexane. The ether was then replaced by toluene and the solution was heated on a steam-bath for one hour. Dilute acetic acid was used to decompose the excess Grignard reagent; the organic layer was separated and dried and the solvent was removed by distillation. The product, bromotricyclohexylgermane, $(C_6H_{11})_3GeBr$, was crystallized from absolute ethanol; m. p. 109°; yield 4 g. (50%).

*Anal.* Calcd.: C, 53.79; H, 8.28; Ge, 18.1. Found: C, 54.46; H, 8.44; Ge, 17.7.

**Preparation of Phenyltricyclohexylgermane.**—A solution of 2 g. (0.005 mole) of bromotricyclohexylgermane in 100 ml. of anhydrous ether was added to 100 ml. of an ether solution of phenyllithium prepared from 10 g. (0.064 mole) of phenyl bromide and an excess of lithium by the general procedure outlined in the preparation of cyclohexyllithium. After the addition of 200 ml. of cyclohexane and the removal of the ether, the reaction mixture was refluxed on a steam-bath for one hour. The excess phenyllithium was destroyed with dilute hydrochloric acid, the organic layer separated and the solvent removed by distillation. The product, phenyltricyclohexylgermane, $(C_6H_{11})_3GeC_6H_5$, was crystallized from absolute ethanol and recrystallized from petroleum ether giving a yield of 1.5 g. (75%); m. p. 210–211°.

*Anal.* Calcd.: C, 72.21; H, 9.60; Ge, 18.2. Found: C, 71.80; H, 9.64; Ge, 18.3.

Attempts to prepare isopropyl- and *o*-tolyltricyclohexylgermane by similar procedures were unsuccessful.

**Hydrolysis of Chlorotricyclohexylgermane.**—A 5% solution of potassium hydroxide in alcohol to which 4 g. of chlorotricyclohexylgermane had been added was refluxed for fifteen minutes with the formation of a white precipitate of potassium chloride. Upon cooling and the addition of an equal volume of water, a white precipitate of tricyclohexylgermanol, $(C_6H_{11})_3GeOH$, was formed. The product was extracted with low-boiling petroleum ether from which it crystallized upon evaporation of the solvent. The yield was practically quantitative: m. p. 175–176°.

*Anal.* Calcd.: C, 63.70; H, 10.12; Ge, 21.4. Found: C, 63.31; H, 10.14; Ge, 21.3.

**Reduction of Chlorotricyclohexylgermane.**—Under anhydrous conditions a solution of 9 g. (0.025 mole) of

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[6] Finholt, Bond, Wilzbach and Schlesinger, THIS JOURNAL, **69**, 2692 (1947).

[7] Nystrom and Brown, *ibid.*, **69**, 1197 (1947).

[8] The possible reduction of the corresponding silanols by this reagent is being investigated.

[9] Kraus and Foster, *ibid.*, **49**, 463 (1927).

[10] Obtained from Metalloy Corporation, Rand Tower, Minneapolis, Minnesota.

[11] Obtained from Research Department, Eagle-Picher Company, Joplin, Missouri.

[12] All melting points are uncorrected.

chlorotricyclohexylgermane in 100 ml. of ethyl ether was added to an excess of lithium aluminum hydride[13] in 300 ml. of ethyl ether. The reaction mixture was maintained at gentle refluxing temperature for one hour and then the excess lithium aluminum hydride was destroyed with dilute sulfuric acid. The organic layer was dried over calcium chloride and the ether was removed by distillation under reduced pressure. The product was crystallized by cooling in an ice-water-bath. The yield of tricyclohexylgermane, $(C_6H_{11})_3GeH$, was 7 g. (87%); m. p. 24-25°.

*Anal.* Calcd.: C, 66.92; H, 10.61; Ge, 22.5. Found: C, 66.42; H, 10.44; Ge, 22.2.

**Reduction of Tricyclohexylgermanol.**—An anhydrous ether solution of 3 g. of tricyclohexylgermanol was added to an ether solution of a large excess of lithium aluminum hydride and the reaction mixture was maintained at the reflux temperature for two hours in the apparatus described above. The excess lithium aluminum hydride was decomposed by dilute sulfuric acid and the ether removed from the organic layer by distillation under reduced pressure. The clear oily liquid, tricyclohexylgermane, was crystallized by cooling in an ice-water-bath; m.p. 24-25°; yield, practically quantitative.

*Anal.* Calcd.: Ge, 22.5. Found: Ge, 22.6.

**Preparation of Tetraphenylgermane.**—A solution of 4.2 g. (0.02 mole) of germanium tetrachloride in 50 ml. of anhydrous ethyl ether was added to 250 ml. of an ether solution of phenyllithium which was prepared from 55.3 g. (0.32 mole) of phenyl bromide and an excess of lithium shot by the procedure described for cyclohexyllithium. The reaction mixture was cooled in an ice-water-bath and stirred during the entire addition. The ether was replaced by toluene and the reaction mixture was held at the reflux temperature for two hours. Following this procedure, the excess phenyllithium was destroyed by adding dilute hydrochloric acid, the mixture was cooled in an ice-water-bath and stirred during the decomposition. The organic layer was separated and the product, tetraphenylgermane, $(C_6H_5)_4Ge$, was crystallized by evaporation of the solvent; yield 90%; m. p. 230-231°.

**Reduction of Di-triphenylgermyl Oxide.**—A solution of 10 g. of tetraphenylgermane in 200 ml. of carbon tetrachloride was treated with an amount in slight excess of an equimolecular proportion of bromine and refluxed for a period of seven hours. The carbon tetrachloride, phenyl bromide and excess bromine were distilled off and the product, bromotriphenylgermane, crystallized from low-boiling petroleum ether. The melting point found was 136°. The bromide was hydrolyzed by boiling with a 5% alcoholic potassium hydroxide solution to give the di-triphenylgermyl oxide; m. p. 182°. A solution of 2 g. of the oxide in 25 ml. of anhydrous ethyl ether was added dropwise to an ether solution containing an excess of lithium aluminum hydride and refluxed for a period of three hours in an apparatus excluding moisture. The excess lithium aluminum hydride was destroyed by dilute sulfuric acid, the organic layer was separated, dried over anhydrous sodium sulfate, and the ether removed by distillation. The product, triphenylgermane, $(C_6H_5)_3GeH$, was crystallized by cooling in an ice-water-bath; m. p. 27°.

*Anal.* Calcd.: Ge, 23.8. Found: Ge, 23.6.

**Reduction of Bromotriphenylgermane.**—This compound was reduced by lithium aluminum hydride using the same procedure as that outlined for bromotricyclohexylgermane giving triphenylgermane, $(C_6H_5)_3GeH$; m. p. 27°.

*Anal.* Calcd.: Ge, 23.8. Found: Ge, 23.9.

**Bromination of Tricyclohexylgermane.**—A solution of 2 g. of tricyclohexylgermane in 50 ml. of ethyl bromide was placed in a 150-ml., two-necked, round-bottom flask fitted for refluxing and bromine added dropwise. The heat of reaction caused vigorous refluxing and the bromine disappeared, accompanied by rapid evolution of hydrogen bromide. After the addition of a slight excess of bromine, the solvent and excess bromine were removed by distillation, and the product, bromotricyclohexylgermane, was crystallized from low-boiling petroleum ether, giving practically a quantitative yield; m. p. 108°.

**Iodination of Tricyclohexylgermane.**—A slight excess of iodine was added to a carbon tetrachloride solution of 2 g. of tricyclohexylgermane and the reaction mixture was held at refluxing temperature until no further evolution of hydrogen iodide gas was observed. Finely powdered metallic silver was added to remove the excess iodine and after removal of excess silver and silver iodide, the carbon tetrachloride was replaced by methanol from which iodotricyclohexylgermane, $(C_6H_{11})_3GeI$, was crystallized; m. p. 99°.

*Anal.* Calcd.: Ge, 16.2. Found: Ge, 16.3.

**Oxidation of Tricyclohexylgermane.**—A solution of 2 g. of tricyclohexylgermane in 100 ml. of carbon tetrachloride in a 200-ml., two-necked, round-bottom flask was refluxed for a period of two hours with a continuous stream of air bubbling through the reaction mixture. The solvent was removed and the product, tricyclohexylgermanol, was recrystallized from low-boiling petroleum ether; m. p. 175-176°.

*Anal.* Calcd.: Ge, 21.4. Found: Ge, 21.5.

Tricyclohexylgermane oxidizes fairly rapidly when left standing in contact with the air.

**Reaction of Tricyclohexylgermanol and Acetyl Chloride.**—A solution of 2 g. of tricyclohexylgermanol in 25 ml. of acetyl chloride was boiled under reflux conditions for one hour. The acetyl chloride and acetic acid were removed by distillation and the product, chlorotricyclohexylgermane, was crystallized from low-boiling petroleum ether; m. p. 96-97°.

*Anal.* Calcd.: C, 60.49; H, 9.31; Ge, 20.3. Found: C, 60.01; H, 9.49; Ge, 20.1.

**Reaction of Tricyclohexylgermanol and Acetic Anhydride.**—A solution of 1 g. of tricyclohexylgermanol in 20 ml. of acetic anhydride was refluxed for a period of two hours. The reaction mixture was then cooled in an ice-water-bath and upon scratching the wall of the flask with a stirring rod, the product crystallized. The fine white crystals were collected in a sintered-glass filter crucible and dried in a pistol using ethanol as the refluxing agent. The product, acetoxytricyclohexylgermane, melted at 82-83°.

*Anal.* Calcd.: C, 63.00; H, 9.53; Ge, 19.1. Found: C, 62.38; H, 9.54; Ge, 19.0.

## Summary

1. The employment of organolithium compounds as alkylating and arylating agents in the preparation of some substituted germanes is described.

2. Possible steric effects were encountered in attempts to introduce the isopropyl, the *o*-tolyl and cyclohexyl group as the fourth group in tricyclohexylgermane.

3. Three new compounds of germanium: tricyclohexylgermane, phenyltricyclohexylgermane and acetoxytricyclohexylgermane have been prepared and some of their properties described.

4. Lithium aluminum hydride has been found to reduce the germanol, tricyclohexylgermanol, to the corresponding germane and di-triphenylgermyl oxide to triphenylgermane.

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(13) Obtained from Metal Hydrides, Inc., Beverly, Mass.