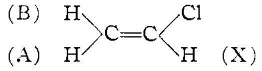
TABLE III

MEDIUM EFFECTS[a] ON CHEMICAL SHIFTS IN 2-CHLOROPROPENE AND VINYL CHLORIDE

Solute	Solvent	δ_A	δ_B	δ_X	$10(2\pi/3)(K - K_S)$[b]	β_A	β_B	β_X
2-Chloropropene[c]	Cyclohexane	0.03	0.00	2.99	...	..	..	..
2-Chloropropene	Acetone	.22	.33	..	−0.312	−0.12	0.02	..
2-Chloropropene	Benzene	.73	.49	3.79	.010	.71	.50	0.80
Vinyl chloride[d]	Cyclohexane	− .23	− .35	−1.15	...	..	..	..
Vinyl chloride	Benzene	.61	.30	−0.36	.01	.85	.66	0.80

[a] Approximate values determined from single measurements in dilute solutions. [b] See ref. 1 for susceptibility data. [c] ABX_3 notation with A proton specified by $|J_{AX}| > |J_{BX}|$. [d] Notation:



since theoretical calculations point to positive, negative or zero values depending on the HCH bond angle.[16] The 2-chloropropene and 2-bromopropene couplings probably are negative by analogy with closely corresponding values in the vinyl; greater electronegativity of the 2-substituent tends to enhance slightly the 1,3 couplings in this series. Opposite trends have been observed in a number of different systems where substitution occurs in a terminal position.[1,2,17]

The vinyl proton shifts show a greater sensitivity to the Y substituent than do the methyl shifts over the series in Table II, and the trends are qualitatively consistent with inductive and mesomeric effects attributable to the 2-substituents. This is particularly apparent in the extreme cases, isopropenyl ether and 2-methylacrolein. No precise correlation is obtained, on the other hand, between the vinyl shifts and Hammett constants[18] for the substituent, so that either these constants are not appropriate in these systems or more probably that other considerations are important in the vinyl proton shieldings. For example, the previously mentioned behavior in methallyl halides points to direct interactions similar to I with nonlinear Y substituents, and long-range anisotropic shieldings may be appreciable even when steric interactions are unimportant.[19] In the case of linear 2-substituents, for example, an anisotropy $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ in the magnetic susceptibility of Y would affect the various protons in approximate proportion to the value of $\Delta\chi r_i^{-3}$ $(3\cos^2\alpha_1 - 1)$ measured from the center of the group and relative to an axis along the =C–Y bond. Choosing Y = –C≡N as a case in point, and approximating the bond-lengths and angles from structural data by Lide[20] and Costain,[21] the effect is predicted to be greater at the vinyl proton *trans* to the substituent than at the *cis* proton, due of course to the angle term. The calculated anisotropic effect is somewhat greater in the methyl group than at either vinyl proton.

The authors wish to acknowledge their sincere appreciation for the support extended to this work by the National Institutes of Health [Research Grant A-2397(C2)] and Schering Corporation, Bloomfield, N. J.

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(16) H. S. Gutowsky, M. Karplus and D. M. Grant, private communication.

(17) A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **25**, 360 (1956).

(18) R. W. Taft, Jr., THIS JOURNAL, **79**, 1045 (1957).

(19) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

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(21) C. C. Costain and B. P. Stoicheff, *ibid.*, **30**, 777 (1959); W. S. Wilcox and J. H. Goldstein, *ibid.*, **22**, 516 (1954).

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, QUARTERMASTER RESEARCH AND ENGINEERING CENTER, U. S. ARMY, NATICK, MASSACHUSETTS]

Equilibrium Constant of Benzaldehyde Sodium Bisulfite

BY JOHN A. SOUSA AND J. DAVID MARGERUM

RECEIVED SEPTEMBER 21, 1959

The ultraviolet spectra of the sodium bisulfite addition complex of benzaldehyde are measured in water as a function of concentration at 13, 23 and 33°. The ultraviolet spectrum of the undissociated complex and the equilibrium constants for the dissociation of the complex in water are calculated. Values for the ΔH, ΔF and ΔS of dissociation are reported. The equilibrium constants are an order of magnitude smaller than those previously reported. The rate of dissociation of the complex is measured at 13° and the rate constants for dissociation and association are calculated. The solid bisulfite complex is found to exist as $C_6H_5CHO \cdot HSO_3Na \cdot {}^1/_2H_2O$.

A previous investigation[1] had determined the equilibrium constant for the formation of the sodium bisulfite complex of benzaldehyde by iodimetric titration of the compound, which was assumed not to be subjected to rapid dissociation as a result of the removal of sodium bisulfite. We have found that the rate of dissociation is fairly rapid. Therefore, the values of the equilibrium constant and the thermodynamic changes involved in the dissociation of benzaldehyde sodium bisulfite which were reported by Gubareva[1] would be expected to be incorrect.

The results of a spectrophotometric procedure for redetermining this thermodynamic data are reported here. It has the advantage that the measurements are made directly on the system without disturbing the equilibrium.

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(1) M. A. Gubareva, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 2259 (1947).

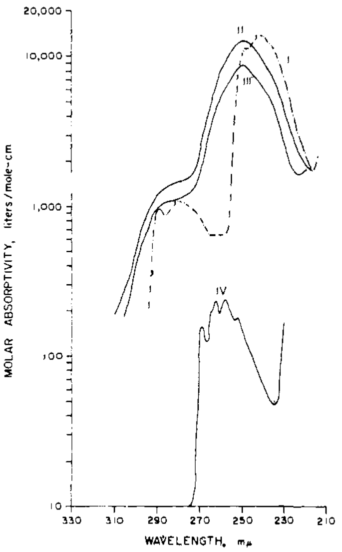
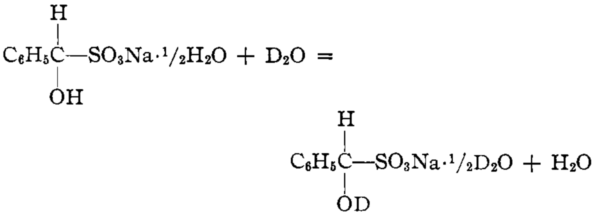


Fig. 1.—Ultraviolet absorption spectra: I, benzaldehyde in isoöctane; II, benzaldehyde in water; III, dilute solution of benzaldehyde sodium bisulfite in water (16.0×10^{-5} m/l.); IV, calculated spectrum of undissociated benzaldehyde sodium bisulfite complex in water.

Experimental

Sodium Bisulfite Addition Complex of Benzaldehyde.—To 0.03 mole of freshly distilled benzaldehyde, 7 cc. of a 40% aqueous solution of sodium bisulfite were added to have a slight excess of benzaldehyde present. The product separated out on standing; it was filtered and washed with ether several times. The solid was dried at 25° in an Abderhalden flask over P_2O_5 at 1 μ for 1.5 hr.

From an elemental analysis for C, H and S (calcd. for $C_6H_5CHO\cdot HSO_3Na\cdot {}^1/_2H_2O$: C, 38.35; H, 3.68; S, 14.63. Found: C, 38.25; H, 3.72; S, 14.64), it was surmised that each mole of complex had $^1/_2$ mole of water of crystallization. To check this, 3.20645 g. of the dry solid complex was mixed with 1.99965 g. of deuterium oxide in one arm of an inverted U-tube, which then was evacuated and allowed to stand for 8 days in order to observe the exchange reaction



$$C_6H_5\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-SO_3Na\cdot {}^1/_2H_2O + D_2O = C_6H_5\overset{\displaystyle H}{\underset{\displaystyle OD}{C}}-SO_3Na\cdot {}^1/_2D_2O + H_2O$$

The final D_2O-H_2O mixture was vacuum distilled from the solid complex upon which it was adsorbed and its density was measured to analyze for the exchange. The purity of the deuterium oxide (Stuart Oxygen Co., Calif., labeled as greater than 99.5% D_2O) was also confirmed by density measurements. A 0.432 ml. aliquot of the water showed a weight change of 0.00514 g., corresponding to 84% of the theoretical weight change calculated for one-half mole of water of crystallization. The vacuum distillation of small amounts of benzaldehyde and sulfur dioxide from the complex along with the water probably accounts for this observation of a smaller weight change than that expected.[2,3]

Rate of Dissociation.—All the spectra were scanned on a Cary, Model 11-MS, automatic recording spectrophotometer. It was noticed that upon dilution of concentrated solutions of benzaldehyde sodium bisulfite the absorbance at 250 mμ changed rapidly with time. This effect was measured accurately for a dilute solution in which the temperature was kept constant at 13°. The initial absorbance was 0.973 in a 1.00 cm. cell at a concentration of 16.29×10^{-5} mole/l. The solution was diluted to 8.20×10^{-5} mole/l. in a 2.00 cm. cell. Actual recording of the absorbance began 18 sec. after dilution, corresponding to the delay in handling and mixing. The change in absorbance was followed until a constant value was reached in approximately 90 sec. corresponding to the re-established equilibrium.

Absorbance of Complex at Equilibrium.—Solutions of known concentrations were prepared by weighing the solid complex on a semi-micro balance and transferring the complex to a 1,000 ml. volumetric flask with water. Final dilution to exactly 1,000 ml. was done immediately. A series of solutions was made up for each temperature. The solutions were immersed in a constant temp. water bath at the desired temperature (13, 23 or 33°). The solutions were transferred to 1.00 cm. glass-stoppered cells as quickly as possible, taking care to keep temperature change to a minimum. Water was circulated through a thermostated cell compartment to maintain constant temperature within ± 0.2°. Sufficient time was allowed for the solutions to establish thermal equilibrium in the cell, as shown by the fact that the absorption max. at 250 mμ showed no further change. It was found that the absorbances were reproducible if measured within a few hours after preparation of the solutions.

Absorptivity of Benzaldehyde.—Since the calculated values of the dissociation constant are dependent upon an accurate value of the molar absorptivity (a_B), redistilled benzaldehyde was measured in both isoöctane and water (curves I & II, Fig. 1). Varying values of a_B in water have been reported in the literature; however, the value obtained in this work, 12,580 l./mole cm. at 250 mμ, agrees with the log ε of 4.10 given by Kenten.[4] The spectrum of benzaldehyde in isoöctane was taken as a check on the purity of the sample. The value obtained in isoöctane, 13,800 l./mole cm. at 241 mμ, agrees with the log ε of 4.14 given by Mariella and Raube.[5] Curve I is shown in Fig. 1 because the shoulder maximum at 248 mμ has not been mentioned in previous reports. This 248 mμ band does not correspond to benzoic acid impurity. It was not changed by attempts to further purify the benzaldehyde. For example, 2.5 μl. of the benzaldehyde showed only a single symmetrical peak on a 8 ft. gas chromatography column (Apiezon L at 168°), and the center cut of this peak when bubbled directly into isoöctane showed the same spectrum as before.

Absorptivity of the Complex.—Even in a saturated solution of the complex the absorbance of benzaldehyde (from dissociation) is so large that it interferes with absorptivity measurements. Therefore, the molar absorptivity of the benzaldehyde sodium bisulfite complex (a_{BS}) was estimated by using concentrated solutions of the complex in the presence of excess sodium bisulfite and measuring the ultraviolet spectra in a 0.0107 cm. CaF_2 cell. Two solutions were run. One was 0.1001 *M* in complex and 0.1004 *M* in $NaHSO_3$, the other was 0.1507 *M* in complex and 0.1508 *M* in $NaHSO_3$. After subtracting for the small absorbance due to the bisulfite, the complex in these solutions was found to have at 250 mμ apparent a_{BS} values of 187 and 175 l./mole cm., respectively. The lower value, from the more concentrated solution, was used in the determinations of the equilibrium constant. From the calculated dissociation constant of 25.1×10^{-5} at 25°, the apparent molar absorptivity of the complex was corrected for the absorptivity due to dissociated benzaldehyde. The corrected spectrum is shown in Fig. 1, curve IV. At 250 mμ the two solutions cited above gave corrected a_{BS} values of 150 and 154 l./mole cm., respectively. The difference between the apparent a_{BS} of 175 and the corrected a_{BS} of 152 is negligible in the calculations of the equilibrium constants.

Results and Discussion

The spectra in the ultraviolet region were used to measure the amount of benzaldehyde present in the equilibrium (A).

If one assumes that at 250 mμ the total absorption is due to only the sum of benzaldehyde, salt and

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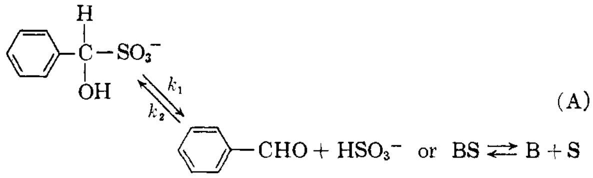
(2) J. A. Sousa and J. D. Margerum, *J. Org. Chem.*, in press.

(3) A. F. Thompson, Jr., and N. H. Cromwell, THIS JOURNAL, **61**, 1374 (1939).

(4) R. H. Kenten, *Biochemical J.*, **55**, 357 (1953).

(5) R. P. Mariella and R. R. Raube, THIS JOURNAL, **74**, 521 (1952).



complex present, then in a 1 cm. cell

$$A = a_B[B] + a_S[S] + a_{BS}[BS]$$

where a_B, a_S and a_{BS} are molar absorptivities of benzaldehyde, salt and complex, respectively. When pure complex is dissolved in water [B] = [S], assuming formation of $SO_3^=$ and H_2SO_3 is negligible. If C is the initial concentration of complex before dissociation, then [BS] = C − [B]. Therefore

$$[B] = \frac{A - a_{BS}C}{a_B + a_S - a_{BS}}$$

and the equilibrium constant is equal to

$$K = \frac{[B]^2}{C - [B]}$$

When $(C - [B])/[B]$ is plotted against [B], the slope of the line is equal to $1/K$.

The absorption spectra of benzaldehyde in water and of a dilute solution of benzaldehyde sodium bisulfite complex are very similar (Fig. 1, curves II and III, respectively) and indicate a high degree of dissociation for the complex in dilute solution. The spectrum of the undissociated complex is shown in curve IV. This was calculated by correcting the spectrum of a concentrated solution of complex in excess sodium bisulfite for the absorption due to bisulfite and dissociated benzaldehyde. The complex has a typical benzenoid absorption, with its maximum absorptivity (240 l./mole cm. at 257.5 mμ) less than 2% of the maximum absorptivity of benzaldehyde.

In dilute solutions of the complex it was found that bisulfite made no significant contribution to the absorption of the equilibrium mixture. A solution of sodium bisulfite whose molarity was 10 fold greater than that of a solution of the complex, showed no appreciable absorption at 250 mμ.

The concentration of benzaldehyde, [B], was calculated from measurements of absorbance at 250 mμ as a function of the initial concentration of the complex (C), shown by the experimental points in Fig. 2. The major assumptions used in these calculations were: (a) the apparent a_{BS} can be used in place of the true molar absorptivity of the complex with negligible error, (b) disproportionation of the bisulfite ion is negligible and (c) absorbance of the bisulfite ion can be ignored. The calculated values of [B] were used to make the plots shown in Fig. 3, where the slopes of the lines are equal to 1/K. The curves drawn through the experimental points in Fig. 2 were calculated from these K's. The calculated curves and the experimental points coincide quite well, which clearly demonstrates the validity of the original assumptions involved. As one approaches infinite dilution, the absorption curves approach that of completely dissociated complex or that of benzaldehyde. The value of K at 25° was used to calculate the corrected spectrum of the complex. The apparent a_{BS} value of 175 l./mole-cm. at 250 mμ is close enough to the corrected value of 152 to cause no significant error in the calculations of K.

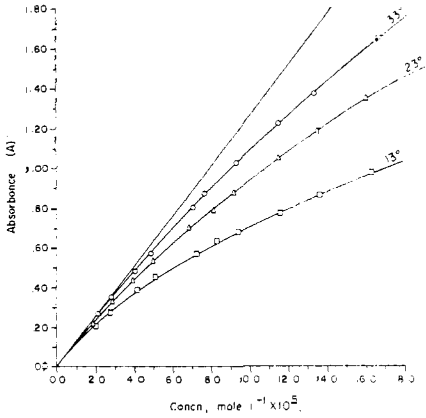


Fig. 2.—Absorbance in water at 250 mμ of benzaldehyde (straight line) and of benzaldehyde sodium bisulfite at three different temperatures. Experimental points are shown with the calculated curves from the appropriate dissociation constants.

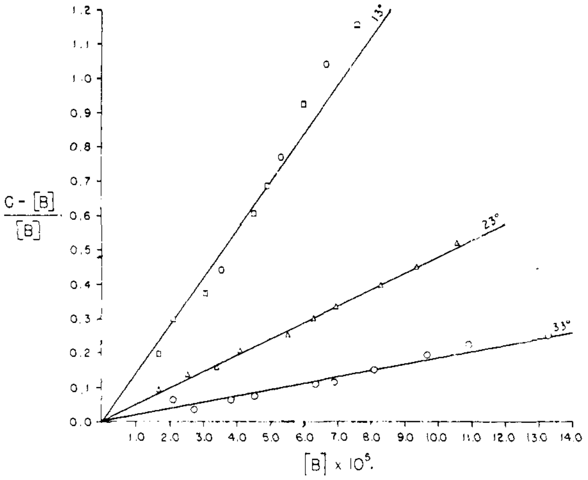


Fig. 3.—Determination of the dissociation constant of benzaldehyde–sodium bisulfite at 13, 23 and 33°.

A plot of log K *vs.* T^{-1} gives a good straight line with a ΔH considerably larger than that previously reported.

The rate of dissociation of the complex was observed by measuring the change in absorbance immediately after dilution and until equilibrium was re-established. Assuming a first and second order reversible reaction[6] it can be shown that a function of the absorbance may be used to determine the rate constant, as shown in Fig. 4 in which the following equation is plotted.

$$\ln\left[\frac{A_\infty - A_0}{A_\infty - A} + \frac{A - A_0}{A_\infty - A}\left(\frac{C - B_\infty}{C}\right)\right] = k_1\left(\frac{2\,C - B_\infty}{B_\infty}\right)t$$

or

$$\log f(A) = \log\,[1.225 + 0.399(A - A_0)] - \log\,(A_\infty - A) = (1.011)k_1t$$

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[6] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 173–174.

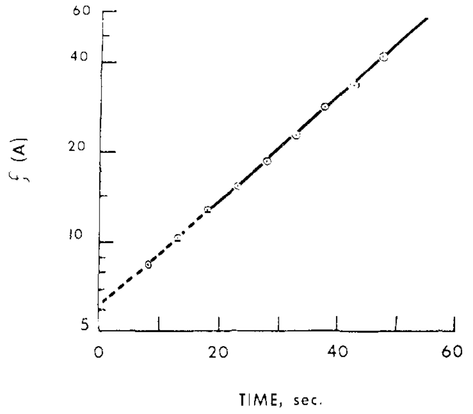

Fig. 4.—Plot for rate constant, k_1, for the dissociation of benzaldehyde–sodium bisulfite in water at 13°. Dotted line corresponds to extrapolated points; k_1 = slope/1.011.

Table I summarizes the values obtained for the equilibrium constant, the thermodynamic functions for the dissociation and the rate constants for dissociation and association. For comparison the values reported by Gubareva at 30° are listed.

TABLE I

T, (°C.)	13	23	33	30 (lit.)[1]
K (l./mole) × 10^5	7.09	21.1	53.8	229
ΔH (kcal./mole)	17.7	17.7	17.7	7.20
ΔS (cal./mole deg.)	42.9	43.0	42.9	12.2
ΔF (kcal./mole)	5.43	4.98	4.58	3.68
k_1 (sec.$^{-1}$)	0.017	...	...	...
k_2 (l./mole sec.)	245	...	...	...

Gubareva also used iodimetric titrations to study the dissociation constants for the bisulfite complexes of a number of aliphatic aldehydes and ketones. He reported K's in the range of 10^{-3} to 10^{-5} and an average value of 7.9 kcal./mole for the ΔH's of dissociation. These values could likewise be subject to error arising from dissociation of the complex during the titration, as may be indicated by the fact that these ΔH's are only about half as large as the ΔH of dissociation found for the benzaldehyde bisulfite complex in this work. Gubareva's ΔH values would indicate that the bond strength of the bisulfite complex is no stronger than that of a strong hydrogen bond. Better values for the equilibrium constants of aliphatic carbonyl bisulfite complexes might be obtained by adding known amounts of the aliphatic carbonyl compound (or its bisulfite salt) to solutions of benzaldehyde sodium bisulfite and using ultraviolet spectra to determine the effect on the concentration of dissociated benzaldehyde. A straightforward, but somewhat cumbersome, relationship exists between the amount of benzaldehyde and the equilibrium constant of the aliphatic carbonyl bisulfite complex in such a system. Error from the absorbance of the aliphatic carbonyl compounds would be negligible since at 250 mμ the molar absorptivities of most of them are only about 0.1% of that of benzaldehyde. This Laboratory does not expect to carry out additional work along these lines.

Acknowledgment.—The authors are indebted to Mr. Carmine DiPietro for the elemental analysis.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DREXEL INSTITUTE OF TECHNOLOGY, PHILADELPHIA, PENNSYLVANIA]

n-Butylhalogermanes with Hydride Bonding[1]

BY HERBERT H. ANDERSON

RECEIVED DECEMBER 1, 1959

Gradually added deficiencies of $HgCl_2$, $HgBr_2$ or I_2 change previously known n-$C_4H_9GeH_3$ into the respective new compounds n-$C_4H_9GeH_2Cl$, n-$C_4H_9GeH_2Br$ and n-$C_4H_9GeH_2I$, all of which have penetrating odors. Similarly, $HgCl_2$, $HgBr_2$ or I_2 change previously known $(n\text{-}C_4H_9)_2GeH_2$—for which there is now a b.p. of 173° under 760 mm.—into new $(n\text{-}C_4H_9)_2GeHCl$, $(n\text{-}C_4H_9)_2GeHBr$ and $(n\text{-}C_4H_9)_2GeHI$. These six new compounds appear to be the first examples of the $RGeH_2X$ or R_2GeHX types in which R is an alkyl group and X is a halogen. Aqueous ammonia and a solution of previously known n-$C_4H_9GeCl_3$ in CCl_4 furnish polymeric white solid $[(n\text{-}C_4H_9GeO)_2O]_n$, which reacts with hot concentrated HBr to give a partial yield of n-$C_4H_9GeBr_3$. Table I lists the properties and analyses of 8 new compounds and presents adequate data on n-$C_4H_9GeCl_3$.

Introduction

Six earlier publications establish the use of halides of certain transitional elements and elements in regular groups in the replacement of hydrogen attached to germanium[2a] in $(C_2H_5)_3GeH$, to tin[2b] in $(C_2H_5)_3SnH$ or to silicon in $(C_2H_5)_3SiH$,[3] $(C_2H_5)_2SiH_2$, n-$C_7H_{15}SiH_3$,[4] cyclo-$C_6H_{11}SiH_3$[5] or n-$C_4H_9SiH_3$.[6]

Gradual addition of $HgCl_2$, $HgBr_2$, AgNCO, AgNCS or I_2 to an excess of the appropriate alkylsilane or dialkylsilane allows relatively straightforward preparation of partially substituted compounds such as n-$C_7H_{15}SiH_2Cl$,[4] $(C_2H_5)_2SiHBr$,[3] cyclo-$C_6H_{11}SiH_2NCO$,[5] cyclo-$C_6H_{11}SiH_2NCS$[5] or n-$C_4H_9SiH_2I$.[6] Moreover, the careful treatment[6] of n-$C_4H_9SiH_3$, b.p. 56°, with $HgCl_2$, $HgBr_2$ or I_2 at either 10 or 22° to obtain n-$C_4H_9SiH_2Cl$, n-$C_4H_9SiH_2Br$ or n-$C_4H_9SiH_2I$, respectively, suggests methods for later preparation of the corresponding compounds n-$C_4H_9GeH_2Cl$, n-$C_4H_9GeH_2Br$ and n-$C_4H_9GeH_2I$.

A recent publication lists the properties of n-$C_4H_9GeH_3$, $(n\text{-}C_4H_9)_2GeH_2$ and a number of other

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[1] Presented at the Third Delaware Valley Regional Meeting of the American Chemical Society, Philadelphia, February, 1960.

[2] (a) H. H. Anderson, THIS JOURNAL, **79**, 326 (1957); (b) **79**, 4913 (1957).

[3] H. H. Anderson, *ibid.*, **80**, 5083 (1958).

[4] H. H. Anderson and A. Hendifar, *ibid.*, **81**, 1027 (1959).

[5] H. H. Anderson, *ibid.*, **81**, 4785 (1959).

[6] H. H. Anderson, *ibid.*, **82**, 1323 (1960).