

formed which is similar to that of neodymium nickel oxide in structure. Table IV indicates this similarity in structure between the two phases; the X-ray pattern for the lanthanum samarium nickel oxide was taken with copper radiation using a 114 mm. Philips powder camera. The pattern for the neodymium nickel oxide was taken with iron radiation using a Norelco G.P. Diffractometer. Lines were resolved with the diffractometer that were not observed on the films taken of the same material. At 70% samarium the pattern is practically identical with that of the 50% composition. The 50% phase can accommodate appreciable substitution of samarium for lanthanum with little apparent change in structure. However, when 85% samarium is reached, the X-ray pattern indicates that most of the product is samarium oxide and nickel oxide.

In the investigation of gadolinium and yttrium

nickel oxides, it has been found that gadolinium or yttrium nickel oxides do not form under the conditions used to prepare LaNiO_3 . Reaction products prepared at 800° , with a sodium carbonate flux, contain only lines of unreacted gadolinium and nickel oxides or yttrium and nickel oxides. When the per cent. substitution of Gd for La is varied from 0 to 100 mole %, the only compounds formed are gadolinium oxide, nickel oxide and lanthanum nickel oxide.

Acknowledgment.—The authors wish to express their appreciation for the financial support given by Research Corporation and the National Science Foundation to Hofstra College where this work was initiated. They also wish to acknowledge the assistance given this study by R. Mazelsky, L. Vogt, A. Craig and L. J. Bailin.

LEXINGTON, MASS.

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

Reactions of Triethyltin Hydride with Inorganic Halides and Oxides

BY HERBERT H. ANDERSON

RECEIVED MARCH 6, 1957

Triethyltin iodide and lithium aluminum hydride react in diethyl ether to yield new liquid triethyltin hydride, b.p. 146° . Triethyltin hydride reduces certain halides and oxides of at least 13 transitional elements and 7 regular group elements either to a lower oxidation state or sometimes to the free element. Some vigorous reactions require gradual addition of a slight deficiency of the inorganic halide in converting triethyltin hydride into a triethyltin halide without forming any diethyltin dihalide. Three different explanations for the 25 reactions in Table I appear possible; heats of formation or free energies per equivalent of available halogen or oxygen in the compounds, also the ionization potentials of the elements, also, although they are not exactly comparable, oxidation potentials in aqueous solution. This paper merely presents the three explanations for the reactions, without lengthy evaluation of the advantages and disadvantages, also theoretical limitations, of each explanation.

This paper is a continuation of an earlier paper on the reactions of triethylgermanium hydride with the salts of transitional elements and with organic haloacids such as CF_3COOH , CCl_3COOH , CBr_3COOH and CH_2ICOOH .¹ In this paper the subject is the reactions of $(\text{C}_2\text{H}_5)_3\text{SnH}$ with halides or oxides of transitional elements and elements in regular groups.

The preparation of $(\text{CH}_3)_3\text{SnH}$, b.p. 59° , from $(\text{CH}_3)_3\text{SnCl}$ and LiAlH_4 ² suggested the one-step preparation of new $(\text{C}_2\text{H}_5)_3\text{SnH}$ reported herein. There is little information on the reactions of alkyltin hydrides in the literature.

Experimental Results

Table I lists 25 reactions of $(\text{C}_2\text{H}_5)_3\text{SnH}$ with halides or oxides of 13 transitional elements and 7 elements in regular groups; these appear to be the first reactions of an alkyltin hydride with halides or oxides of elements in regular groups. A median yield of 88% in Table I is based upon the starting material present in the lesser amount. Some of these reactions, especially those with SnCl_2 or HgO , may prove of preparative value on a larger scale.

Gradual addition of the halide or HgO to a slight excess of $(\text{C}_2\text{H}_5)_3\text{SnH}$ is necessary to ensure formation of the monosubstitution product $2(\text{C}_2\text{H}_5)_3\text{SnH} + \text{PdCl}_2 \rightarrow 2(\text{C}_2\text{H}_5)_3\text{SnCl} + \text{Pd} + \text{H}_2$ rather

than the disubstitution product $2(\text{C}_2\text{H}_5)_3\text{SnH} + 2\text{PdCl}_2 \rightarrow 2(\text{C}_2\text{H}_5)_2\text{SnCl}_2 + 2\text{Pd} + \text{H}_2 + \text{C}_4\text{H}_{10}$. Other experiments here show the related unpublished reaction $2(\text{C}_2\text{H}_5)_4\text{Sn} + \text{PdCl}_2 \rightarrow 2(\text{C}_2\text{H}_5)_3\text{SnCl} + \text{Pd} + \text{C}_4\text{H}_{10}$.

Certain compounds do not react with $(\text{C}_2\text{H}_5)_3\text{SnH}$ at a perceptible rate. No reaction is expected using BaCl_2 or TlCl —considering oxidation potentials, ionization potentials or heats of formation—and none occurs. Expected reactions with KClO_3 (reduction to KCl expected) or K_2CrO_4 do not occur, although CrO_2Cl_2 does react.

At 25° benzene solutions of $(\text{C}_2\text{H}_5)_3\text{SnH}$ react fairly rapidly with PdCl_2 , AsCl_3 , HgBr_2 and SnCl_4 ; an excess of the last compound yields SnCl_2 as an instantaneous white precipitate. However, K_2PtCl_6 does not react, even in one minute of reflux in benzene solution.

Discussion

Four previous publications are vitally related to an explanation of the probably partly ionic $(\text{C}_2\text{H}_5)_3\text{Sn}^\delta + \text{H}^{\delta-}$, which yields a definitely partly ionic chloride $(\text{C}_2\text{H}_5)_3\text{Sn}^\delta + \text{Cl}^{\delta-}$. Numerous reactions of $(\text{CH}_3)_2\text{SnCl}_2$ in aqueous solution suggest that $(\text{CH}_3)_2\text{SnCl}_2$ resembles SnCl_2 rather than SnCl_4 ; the ion $(\text{CH}_3)_2\text{Sn}^{+2}$ evidently resembles Sn^{+2} .³ The fewer the number of halogen atoms in an ethyltin chloride molecule, the stronger the Sn-Cl bond

(1) H. H. Anderson, *THIS JOURNAL*, **79**, 326 (1957).

(2) A. E. Finholt, *et al.*, *ibid.*, **69**, 2692 (1947).

(3) E. G. Rochow, *et al.*, *ibid.*, **78**, 3099 (1953).

TABLE I
 REACTIONS OF $(C_2H_5)_3SnH$, 1.00 G./RUN, WITH INORGANIC HALIDES AND OXIDES

Salt or oxide at start			Reaction products				
Compd.	Wt., g.	Reflux, min.	Compd.	Chief product B.P., °C.	Wt., g.	Yield, %	Other products
CuBr ₂ ^a	0.96	10	$(C_2H_5)_3SnBr$	224	1.19	91 ^b	CuBr, ^c Cu, ^d H ₂ , $(C_2H_5)_2SnBr_2$ ^d
AgBr ^a	.85	2	$(C_2H_5)_3SnBr$	221	1.07	82 ^b	Ag, H ₂
KAuCl ₄	.60	10	$(C_2H_5)_3SnCl$	209	1.08	94	Au, KCl, H ₂
ZnO	.22	55	$[(C_2H_5)_3Sn]_2O$	250	0.41	40	Zn, H ₂
CdCl ₂	.43	40	$(C_2H_5)_3SnCl$	208	.48	47	Cd, H ₂
HgCl ₂ ^a	.61	5	$(C_2H_5)_3SnCl$	213	.84	78	Hg, Hg ₂ Cl ₂ , ^d H ₂
HgO ^a	.85	3	$[(C_2H_5)_3Sn]_2O$	273	.93	91	Hg, H ₂
TiCl ₄ ^a	.44	15	$(C_2H_5)_3SnCl$	208	.60	55	TiCl ₃ , ^e H ₂
VOCl ₃ ^a	.41	5	$(C_2H_5)_3SnCl$	205	.60	61	VOCl ₂ , ^f H ₂
V ₂ O ₅	.14	30	$[(C_2H_5)_3Sn]_2O$	274	.91	88	V ₂ O ₂ , ^f H ₂
CrO ₂ Cl ₂ ^a	.35	3	$(C_2H_5)_3SnCl$	210	.84	78	Cr ₂ O ₃ , ^{c,h} H ₂ , H ₂ O ^d
KMnO ₄	.35	30	$[(C_2H_5)_3Sn]_2O$	272	.90	87	KOH, MnO ₂ , ^{e,i} H ₂ O ^d
Fe ₂ O ₃	.15	45	$[(C_2H_5)_3Sn]_2O$	272	.62	60	Fe, H ₂ , H ₂ O ^d
PdCl ₂ ^a	.31	2	$(C_2H_5)_3SnCl$	210	.80	97	Pd, H ₂
K ₂ PtCl ₆ ^a	.87	4	$(C_2H_5)_3SnCl$	209	0.85	75	KCl, Pt, H ₂
GeCl ₄ ^a	.26	10	$(C_2H_5)_3SnCl$	211	1.13	97	Ge, GeH ₄ , ^{d,j} H ₂
SnCl ₄ ^a	.31	4	$(C_2H_5)_3SnCl$	211	1.08	94	Sn, H ₂
SnCl ₂	.51	20	$(C_2H_5)_3SnCl$	210	1.12	96	Sn, H ₂
PbCl ₂	.64	30	$(C_2H_5)_3SnCl$	209	1.05	95	Pb, H ₂
PbO	.57	30	$[(C_2H_5)_3Sn]_2O$	273	0.90	87	Pb, H ₂ , H ₂ O ^d
AsCl ₃ ^a	.25	3	$(C_2H_5)_3SnCl$	210	1.00	99	As, H ₂
As ₄ O ₆	.20	22	$[(C_2H_5)_3Sn]_2O$	271	0.66	63	As, H ₂ , H ₂ O ^d
SbCl ₃ ^a	.34	5	$(C_2H_5)_3SnCl$	210	1.09	99	Sb, H ₂
BiCl ₃	.51	2	$(C_2H_5)_3SnCl$	211	1.08	93	Bi, H ₂
S ₂ Cl ₂ ^a	.30	3	$(C_2H_5)_3SnCl$	210	0.91	84	$[(C_2H_5)_3Sn]_2S$, ^k H ₂ S, H ₂

^a Gradual addition of this reagent to $(C_2H_5)_3SnH$. ^b All yields based upon the starting material present in lesser amount. ^c Compound insoluble in water. ^d Compound present in small amount. ^e Solid a mixture of violet and brownish-black, perhaps containing a little TiCl₂. ^f Grey-brown solid which dissolved in HCl to give green solution and hydrogen. ^g Dark grey solid which dissolved in HCl to give green solution of VCl₂. ^h Light green solid. ⁱ Brown solid which liberated chlorine with HCl. ^j Combustion of the exit gas in a limited amount of air produced a little brownish solid Ge. ^k High-boiling liquid containing sulfide. Weight 0.17 g., or 16% yield. See G. S. Sasin, *J. Org. Chem.*, 18, 1142 (1953).

appears to be, with a progressive decrease in the mobility of chlorine in the order $(C_2H_5)_3SnCl > (C_2H_5)_2SnCl_2 > C_2H_5SnCl_3 > SnCl_4$ in reactions such as ⁴ $[(C_2H_5)_3Sn]_2O + (C_2H_5)_2SnCl_2 \rightarrow 2(C_2H_5)_3SnCl + [(C_2H_5)_2SnO]_n$. There is a progressive decrease in the reaction extent of organogermanium oxides with weak acids⁵ in the series $[(C_2H_5)_3Ge]_2O$, $[(C_2H_5)_2GeO]_4$ and $[(C_2H_5)_2GeO]_n$ as the oxygen content increases. The molar conductivity of $(C_2H_5)_3SnOH$ at infinite dilution is 0.45, that of a weak base,⁶ while the strong base NaOH has a value of 208.

A careful study of the reactions of $(C_2H_5)_3SnH$ with 25 halides or oxides in Table I, but not with BaCl₂ or TiCl₄, suggests the following four possible conclusions about the reactivity of $(C_2H_5)_3SnH$. (Stoichiometry limits the extent of reduction¹ in several instances, such as the reduction of CuBr₂ mainly only to CuBr herein.)

1. Heats of formation ΔH —a fairly good criterion—(and for the most part available free energies) per equivalent of halogen or oxygen are in agreement with most of the successful reactions of $(C_2H_5)_3SnH$, especially the reactions with CrO₂Cl₂ and KMnO₄. However, heats of formation fail to predict the successful reactions with ZnO, CdCl₂ or SnCl₂, while a partial reaction with PbCl₂ is probable on this basis.

2. Ionization potentials seem to be a good criterion whether $(C_2H_5)_3SnH$ will react with given halide or oxide. The ionization potential⁷ for the removal of the first electron from tin—the first ionization potential—is 7.332 e.v., corresponding evidently to Sn(I). This criterion alone predicts the highly-successful reaction with Sn(II) in Table I, $2(C_2H_5)_3SnH + SnCl_2 \rightarrow 2(C_2H_5)_3SnCl + Sn + H_2$, and the reactions with ZnO and CdCl₂, which both give yields a little under 50%. Ionization potentials predict some reduction of KMnO₄, but fail to account adequately for the successful reactions with VOCl₃ or CrO₂Cl₂.

3. Oxidation potentials in aqueous solutions E^0 , not strictly comparable to the conditions in this paper, as before,¹ remain a fair criterion whether $(C_2H_5)_3SnH$ will react with a given halide or oxide. The available E^0 for Sn(0) to Sn(II) does not correspond to the conversion of $(C_2H_5)_3SnH$ to $(C_2H_5)_3SnCl$; this conversion corresponds to an unavailable E^0 for Sn(0) to Sn(I), essentially. Thus application of E^0 for Sn(0) to Sn(II) to the reactions of $(C_2H_5)_3SnH$ fails to predict the high yields with SnCl₂ or PbCl₂, and also the moderate yields with ZnO or CdCl₂.

4. Predictions for untried reactions based on ionization potentials, oxidation potentials or heats of formation per equivalent of available chlorine

(4) H. H. Anderson, *J. Org. Chem.*, 19, 1766 (1954).

(5) H. H. Anderson, *THIS JOURNAL*, 72, 2089 (1950).

(6) F. Hein and H. Meininger, *Z. anorg. Chem.*, 146, 95 (1925).

(7) C. E. Moore, "Atomic Energy Levels," Circular of National Bureau of Standards, No. 467, June 15, 1949; J. Sherman, *Chem. Revs.*, 11, 93 (1932).

indicate that $(C_2H_5)_3SnH$ should react with $SeCl_4$, $TeCl_4$, $RuCl_2$ or K_2OsCl_6 to yield $(C_2H_5)_3SnCl$ and the free elements Se, Te, Ru and Os.

Apparently $(C_2H_5)_3SnH$ is more reactive than $(C_2H_5)_3GeH$ ¹ is, since the latter reacts comparatively slowly with the oxygen in the air, and not at all with $CdCl_2$ or CH_3COOH . Oxygen in the air reacts more rapidly with the organotin hydride $2(C_2H_5)_3SnH + O_2 \rightarrow 2(C_2H_5)_3SnOH$ followed by loss of water at elevated temperature (if such be available) $2(C_2H_5)_3SnOH \rightarrow [(C_2H_5)_3Sn]_2O + H_2O \uparrow$. Acetic acid reacts rapidly in reflux $(C_2H_5)_3SnH + CH_3COOH \rightarrow (C_2H_5)_3SnOCOCH_3 + H_2$.

Experimental

Equipment as before¹ included distilling units with ground joints, also transfer micropipets, a pycnometer for density and some very small distilling units.

Triethyltin Hydride.—This compound reacts with the oxygen in air, and therefore a minimum amount of air should be present during the preparation of the compound. Gradual addition of 133 g. of $(C_2H_5)_3SnI$ over 15 min. to a solution of 18 g. of $LiAlH_4$ in 200 ml. of dry ether was followed by 90 minutes of reflux. After slow addition of water until there were two layers, there followed slow addition of a slight deficiency of 6 *M* H_2SO_4 , then shaking and separation of layers soon. Next came drying with Na_2SO_4 in a closed container, followed by filtration and then distillation of the ether. A first fractional distillation under 47 mm. pressure furnished 40 g. of crude $(C_2H_5)_3SnH$ boiling at approximately 70° and left 42 g. of crude $[(C_2H_5)_3Sn]_2O$ in the residue; redistillation of the $(C_2H_5)_3SnH$ furnished a center fraction boiling at 69–70° under 47 mm. pressure, later used in all measurements. An actual yield of 48% as $(C_2H_5)_3SnH$ might have been higher in the absence of oxygen, which caused formation of some $[(C_2H_5)_3Sn]_2O$. All samples were stored in sealed tubes with a minimum amount of air present; upon standing one month some samples developed a little pressure, but no metallic tin formed. At first $(C_2H_5)_3SnH$ had the b.p. 146° under 760 mm. pressure, but the b.p. in air rose to 149° within one minute of reflux and the inoffensive odor of pure $(C_2H_5)_3SnH$ changed in part to the disagreeable odor of $[(C_2H_5)_3Sn]_2O$. *Anal.* Calcd. for $(C_2H_5)_3SnH$: mol. wt., 206.9; Sn, 57.5; hydride H, 0.49. Found: mol. wt. (naphthalene), 223; Sn, 57.1; hydride H, 0.49. Found: mol. wt. (naphthalene), 223; Sn, 57.1; hydride H, 0.49. Also, pure $(C_2H_5)_3SnH$ had a

weak, inoffensive odor, d^{20}_4 1.259 and n^{20} 1.472₆. Determination of hydride hydrogen employed a gentle 3 minute reflux with excess glacial acetic acid followed by collection and measurement of the volume of hydrogen in the gas buret, after the return of the system to room temperature with much agitation to ensure saturation of the gas with water vapor; the equation is at the end of the Discussion. This analytical data and the 25 reactions in Table I support the formula $(C_2H_5)_3SnH$.

Starting materials other than commercial products included anhydrous $CdCl_2$ and $SnCl_2$ made from commercial hydrates, and included special preparations of $GeCl_4$, $VOCl_3$ and CrO_2Cl_2 . All the solids were dry and powdered.

Reactions of $(C_2H_5)_3SnH$.—These had some alterations on the methods used with $(C_2H_5)_3GeH$.¹ Slow reactions of $(C_2H_5)_3SnH$ in reflux with ZnO , Fe_2O_3 , PbO and As_2O_3 permitted addition of the hydride to the inorganic oxide. Gradual addition of the inorganic halide or HgO was necessary in 14 instances. Powdered $KMnO_4$ reacted satisfactorily with $(C_2H_5)_3SnH$ in the absence of a solvent to furnish a yield of $[(C_2H_5)_3Sn]_2O$ superior to that obtained with $(C_2H_5)_3GeH$ in acetone.¹ Table I lists the individual reactions, with yields based upon the starting material present in the lesser amount.

Identification of the Chief Organotin Product in Table I.—This follows the separative methods for the products from $(C_2H_5)_3GeH$.¹ Usually a first fractional distillation separated the chief organotin product from excess $(C_2H_5)_3SnH$, while a second or third fractional distillation produced a sufficiently pure fraction of the chief organotin compound to allow determination of the boiling point and refractive index. Volumes, boiling points and refractive indices of the various liquid fractions established the identities and amounts of the compounds present. Accepted b.p.'s and refractive indices follow: $(C_2H_5)_3SnCl$, b.p. 210°, n^{20} 1.507; $(C_2H_5)_3SnBr$, b.p. 224°, n^{20} 1.5281; $[(C_2H_5)_3Sn]_2O$, b.p. 272°. Recent unpublished measurements by the present author furnished d^{20}_4 1.401 and n^{20} 1.501₀ for center-fraction $[(C_2H_5)_3Sn]_2O$.

Identification of Other Products in Table I.—Visual observations sufficed to establish the formation of the metals and also the condensation of a little water. Other tests included the insolubility in water, the inflammability of hydrogen, colors, the odor of hydrogen sulfide, the colors of the vanadium compounds obtained upon dissolving in hydrochloric acid, or the burning of the exit gas to deposit a small amount of brownish germanium.

(8) E. Krause and A. V. Grosse, "Die Chemie der metallorganischen Verbindungen," Photolithoprint, Edwards Bros., Ann Arbor, Mich., 1943, pp. 327, 336, 743.

PHILADELPHIA 4, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEFENSE RESEARCH LABORATORY OF THE UNIVERSITY OF TEXAS]

Some Compressibility Relations of 1,2-Dichloro-1,1-difluoroethane

BY MARVIN LEE DEVINEY, JR.,¹ WITH W. A. FELSING²

RECEIVED APRIL 3, 1957

Compressibility data for liquid 1,2-dichloro-1,1-difluoroethane in the range 80 to 225° are given. Vapor pressures are given both in equation form and tabular form for the range 110 to 220°.

Introduction

Compressibility data on numerous hydrocarbons have been determined in and presented³ from this Laboratory but this investigation is the first dealing with the compressibilities of a halogenated hydrocarbon. 1,2-Dichloro-1,1-difluoroethane may prove useful in refrigeration and air-conditioning applications.

(1) Special Problems Laboratory, Chemical Plant, Celanese Corporation of America, Bishop, Texas.

(2) Deceased, October 5, 1952.

(3) H. O. Day with W. A. Felsing, *THIS JOURNAL*, **74**, 1951 (1952); ref. 1.

Previous Investigations.—No previous compressibility data for this compound have been found in the literature. Henne and Hubbard⁴ have reported data on the freezing point, the boiling point, the density at 20° and the refractive index. Harmon⁵ presented boiling point and refractive index data. However, pressure-volume-temperature relations have been reported by Benning and McHarness⁶ on four similar halogenated com-

(4) A. L. Henne and D. M. Hubbard, *ibid.*, **58**, 404 (1936).

(5) Jesse Harmon, U. S. Patent 2,399,024 (April 23, 1946).

(6) A. F. Benning and R. C. McHarness, *Ind. Eng. Chem.*, **52** 698 (1940)