give an additional 13.1 g. of solid product. The $(Me_3SiCH_2)_2SnBr_2$ so obtained was dissolved in 30–60° petroleum ether, treated with decolorizing charcoal, and recrystallized at −78°.

(7) **Cleavage with Trifluoroacetic Acid.**—To 26.5 g. (0.065 mole) of III in a three-necked flask, equipped with a mechanical stirrer, a dropping funnel and a reflux condenser, was added 7.4 g. (0.065 mole) of CF_3CO_2H. The open end of the condenser was connected to a cold trap in order to catch any volatile products. A mildly exothermic reaction developed as the acid was added. The mixture was stirred at room temperature for one-half hr., then at 60° for 2 hr. and finally for 3 hr. at 80°. The reaction mixture solidified on cooling to give a waxy semi-solid material. Recrystallization from 30–60° petroleum ether yielded 15.4 g. of white crystals, m.p. 62–63.4°, identified by analysis as di-*n*-butyl-(trimethylsilylmethyl)-tin trifluoroacetate. Dilution of the liquid in the cold trap with 20 ml. of xylene, followed by fractional distillation yielded 1.5 g. of tetramethylsilane.

(8) **Cleavage with Mercuric Bromide.**—A solution of 5.58 g. (0.0155 mole) of mercuric bromide in 50 ml. of absolute ethanol was added to 5.0 g. (0.0155 mole) of II. The mixture was refluxed for 45 hr. A small amount of reduction occurred, as evidenced by the presence of a few small droplets of mercury in the bottom of the reaction flask. Typical white, glistening RHgX-type crystals formed when the reaction mixture was cooled. These were filtered and the filtrate was concentrated to about one-half of its original volume and cooled again to give additional solid. In this manner 4.3 g. of CH_3HgBr, m.p. 157–158°, a yield of 94%, was obtained. A m.p. of 161.1° has been reported[13] for pure CH_3HgBr.

Anal. Calcd. for CH_3BrHg: Hg, 67.87. Found: Hg, 67.73.

(9) **Reactions of $(Me_3SiCH_2)_2SnX_2$ Compounds.** (a) $(Me_3SiCH_2)_2SnO$.—Solutions of 1.12 g. (0.02 mole) of KOH in 10 ml. of water and 4.5 g. (0.01 mole) of $(Me_3SiCH_2)_2SnBr_2$ in 15 ml. of diethyl ether were shaken together in a separatory funnel. The ethereal layer was diluted with 30–60° petroleum ether and separated from the aqueous phase. Evaporation of the organic solvents gave white amorphous solid, polymeric $(Me_3SiCH_2)_2SnO$, which was dried in the steam oven.

Anal. Calcd. for $C_8H_{22}OSi_2Sn$: C, 31.08; H, 7.17. Found: C, 30.95; H, 7.16. The polymeric oxide softens and melts over the range 145–160°.

(b) $(Me_3SiCH_2)_2SnS$.—$(Me_3SiCH_2)_2SnI_2$, 5.0 g. (0.0091 mole), was dissolved in ethanol and the solution was saturated with H_2S gas. No precipitate resulted. To the solution then was added 2.2 g. (0.0091 mole) of $Na_2S{\cdot}9H_2O$ and the H_2S addition was continued until white solid came out of solution. This was washed repeatedly with cold ethanol to give 2.0 g. of product. Recrystallization from ethanol gave as a small first fraction very fluffy white solid, melting range, 150–165°.

Anal. Calcd. for $C_8H_{22}SSi_2Sn$: C, 29.54; H, 6.82. Found: C, 29.37; H, 6.69.

The more soluble portion, obtained as a second fraction after concentration of the alcoholic solution, was obtained in the form of large, well-defined crystals, m.p. 74.4–75.5°.

Anal. Found: C, 29.81; H, 6.71.

Thus both fractions consist of the desired sulfide. The second fraction apparently is mainly composed of the trimer (mol. wt. 976) and tetramer (mol. wt. 1301), since the molecular weight of this fraction was determined to be 1105. It is likely that the less soluble portion is a higher polymer.

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Cambridge 38, Massachusetts

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[Contribution from the Mallinckrodt Chemical Laboratory at Harvard University]

Vinyl Derivatives of the Metals. VI. Preparation, Properties and Some Reactions of Trivinyl Compounds of Group V Elements[1,2]

By Ludwig Maier, Dietmar Seyferth, F. G. A. Stone and Eugene G. Rochow

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Trivinyl compounds of Group V elements have been prepared by the reaction between vinyl Grignard reagent and the appropriate trihalide. Some physical properties of these trivinyl derivatives are reported, and several new addition compounds of the type $[(CH_2{:}CH)_3RM^V]X$ are described. The ability to form "onium" type adducts decreases in passing from trivinylphosphine to trivinylbismuth. Trivinylarsine and -stibine form complex compounds $[(CH_2{:}CH)_3M^V]_2PtCl_2$. Thermal decomposition of trivinylarsine- and trivinylstibine diiodides yielded the corresponding divinyliodo derivatives. Redistribution reactions occur when trivinylarsine and trivinylstibine are mixed with their respective trichlorides or tribromides. In this manner the new compounds $(CH_2{:}CH)AsBr_2$, $(CH_2{:}CH)_2AsBr$, $(CH_2{:}CH)AsCl_2$, $(CH_2{:}CH)_2SbBr$ and $(CH_2{:}CH)_2SbCl$ were obtained, as well as certain *n*-butyl derivatives, *n*-$BuAs(CH{:}CH_2)_2$, *n*-$Bu_2AsCH{:}CH_2$ and *n*-$Bu_2SbCH{:}CH_2$. Vinylhaloarsines were also obtained by mixed redistribution reactions using *n*-$Bu_2Sn(CH{:}CH_2)_2$ and arsenic trichloride or tribromide. When mixed in the correct proportions, arsenic tribromide and triethylarsine also react exothermally giving ethyldibromoarsine.

The first vinyl derivatives of phosphorus and arsenic, prepared by dehydrohalogenation of β-bromoethylphosphonium and arsonium salts, were reported by Hofmann 97 years ago.[3] Vinylphosphorus compounds of the type $CH_2{:}CHP(O)(OR)_2$ have been described more recently,[4] and some sub-

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[1] Paper V in this series: D. Seyferth, *J. Org. Chem.*, **22**, 1252 (1957).

[2] For a preliminary communication see: L. Maier, D. Seyferth, F. G. A. Stone and E. G. Rochow, *Z. Naturforsch.*, **12b**, 263 (1957).

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stituted vinylphosphonic acids and esters have been reported in journal[5] and in patent[6] literature. A separate class of considerable importance is that of the β-chlorovinyl compounds of arsenic[7] and antimony,[8] made by the action of acetylene on arsenic trichloride and antimony pentachloride, respectively.

Continuing our study of vinyl derivatives of metals and metalloids,[9] we have now prepared the trivinyl compounds of phosphorus, arsenic, antimony and bismuth, and have investigated their physical properties and some of their chemical reactions. These new compounds are of particular interest, since they make possible a study of the consequences of attaching an α-alkenyl group to electron donor atoms, just as the preparation of trivinylborane has made possible investigation of the consequences of attaching α-alkenyl groups to an electron acceptor atom.[10]

The trivinyl derivatives of the Group V elements were prepared by reaction of the appropriate halide with vinylmagnesium bromide in tetrahydrofuran[11]

$$3CH_2{:}CHMgBr + X_3M^V \longrightarrow (CH_2{:}CH)_3M^V + 3MgBrX$$

Special techniques were required for the reaction between phosphorus trichloride and the Grignard solution. Phenyldivinylphosphine was similarly obtained by Grignard vinylation of phenyldichlorophosphine.

The four trivinyl compounds, liquids at ordinary temperatures (*cf.*, Table I), are oxidized easily in air. Trivinylstibine and trivinylbismuth are spontaneously inflammable. In the absence of air, however, thermal stability is relatively high. Trivinylarsine may be refluxed under nitrogen at its normal boiling point without decomposition, while a sample of trivinylbismuth was unaffected when heated at reduced pressure at 100° for several hours. However, over a period of months at room temperature some decomposition of trivinylbismuth occurred.

TABLE I

PHYSICAL PROPERTIES OF TRIVINYL COMPOUNDS OF GROUP VB ELEMENTS

Compound	Vapor pressure constants[a] *A*	*B*	B.p.,[b] °C. (760 mm.)	F.p.,[c] °C.	Δ*H* vap. at b.p. (kcal./mole)	Trouton constant (cal./deg. mole)
$(CH_2{:}CH)_3P$	1763	7.399	117.0	−110.0	8.06	20.7
$(CH_2{:}CH)_3As$	1857	7.489	129.8	−125.6	8.49	21.1
$(CH_2{:}CH)_3Sb$	2013	7.639	149.9	−157.0	9.21	21.8
$(CH_2{:}CH)_3Bi$	2499	8.674	158.1	−124.5	11.43	26.5

[a] Constants for the equation $\log_{10} p_{\text{mm.}} = B - A/T$. [b] Found by extrapolation of vapor pressure equations. [c] Stock magnetic plunger method.

The ability to form addition compounds with methyl iodide, ethyl iodide and vinyl bromide decreases in passing from trivinylphosphine to trivinylbismuth, *viz.*

	$(CH_2{:}CH)_3$-P	$(CH_2{:}CH)_3$-As	$(CH_2{:}CH)_3$-Sb	$(CH_2{:}CH)_3$-Bi
CH_3I	+	+	+	−
C_2H_5I	+	+	−	−
$CH_2{:}CHBr$	+	−	−	−

where the plus signs indicate formation of solid adducts, and the negative signs no evident reaction even at 100°. This observed trend parallels the tendency of trialkyl derivatives of the Group V elements to form adducts of the "onium" type. Trivinylarsine similarly adds anhydrous hydrogen chloride to give white, crystalline trivinylarsonium chloride, $[(CH_2{:}CH)_3HAs]\,Cl$.

As would be expected, trivinylarsine and -stibine form complex compounds of the type $[(CH_2{=}CH)_3M^V]_2PtCl_2$ with platinum(II) chloride. With trivinylstibine the *cis*-isomer should precipitate, because no *trans*-isomers $(R_3Sb)_2PtX_2$ are known in the solid state.[12] Furthermore, as formation of *cis*-isomer is favored by attaching electronegative groups to the ligand atom,[12] *cis*-compound formation would be preferred also in the case of trivinylarsine, owing to the electronegativity of the vinyl groups.

Trivinylphosphine was found to combine in a 1:1 ratio with carbon disulfide, forming a red solid, and with boron trifluoride to form a white solid adduct.

Trivinylarsine and trivinylstibine react with iodine to give trivinylarsine- and trivinylstibine diiodides. The latter undergo thermal decomposition yielding vinyl iodide and the corresponding divinyliodo derivatives, *e.g.*

$$(CH_2{:}CH)_3Sb + I_2 \longrightarrow (CH_2{:}CH)_3SbI_2 \longrightarrow (CH_2{:}CH)_2SbI + CH_2{:}CHI$$

Thermal decomposition of methyltrivinylstibonium iodide results in cleavage of methyl iodide to give the parent trivinyl compound.

The trivinyl compounds of arsenic and antimony undergo redistribution when mixed with the trichlorides or tribromides of the respective elements

$$(CH_2{:}CH)_3As + 2AsBr_3 \longrightarrow 3CH_2{:}CHAsBr_2$$

$$2(CH_2{:}CH)_3Sb + SbCl_3 \longrightarrow 3(CH_2{:}CH)_2Sb$$

Moderate yields of either the monovinyl or divinyl derivatives can be obtained from these exothermic reactions by mixing the reactants in the correct proportions. Trivinylphosphine and phosphorus trihalides react very vigorously at room temperature; however, only decomposition products (black solids) result. No volatile products were isolated. During these redistribution reactions it sometimes was impossible to separate the products because their boiling points were too close to each other to permit fractional distillation. Thus separation by distillation of the reaction mixture containing the compounds $(CH_2{:}CH)_2AsCl$, $CH_2{:}CHAsCl_2$ and $AsCl_3$ proved to be impossible. Separation was achieved successfully, however, by alkylation of the entire reaction mixture with *n*-butylmagnesium bromide, thereby giving instead a mixture of $(CH_2{:}CH)_2$-

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AsBu-*n*, *n*-$Bu_2AsCH{:}CH_2$ and *n*-Bu_3As, which could be easily separated by distillation. In a similar manner *n*-$Bu_2SbCH{:}CH_2$ and *n*-Bu_3Sb were obtained from a mixture of $CH_2{:}CHSbBr_2$ and $SbBr_3$.

Redistribution reactions analogous to those described above are known for triarylarsines[13] and tribenzylarsine,[14] but they do not appear to have been reported for trialkyl derivatives. In order to determine whether the redistribution reaction is general for all triorganoarsenic compounds, the reaction of arsenic tribromide with triethylarsine was investigated. A good yield of ethyldibromoarsine was in fact obtained from the exothermic reaction. The redistribution reaction is thus a good alternate to the previous methods for the synthesis of compounds of the type $RAsX_2$ and R_2AsX,[15] although the preparation of ethyldichloroarsine, -phosphine and -stibine by ethylation of the respective trichlorides with tetraethyllead[15c] is attractive because of the ready availability of this particular lead alkyl. Redistribution of trimethylbismuth with bismuth halides has been described,[16] but this reaction has only been reported for triarylstibines.[13,17]

We have shown previously[9b] that vinylmercuric halides can be made by treating the corresponding mercuric halide with an alkylvinyltin compound. This "mixed" redistribution reaction has been extended to the preparation of some vinyl derivatives of Group V halides. It was most successful in the synthesis of vinyldibromoarsine and divinylbromoarsine; a yield of 81% being obtained in the latter case.

$$n\text{-}Bu_2Sn(CH{:}CH_2)_2 + AsBr_3 \xrightarrow{95°} n\text{-}Bu_2SnBr_2 + (CH_2{:}CH)_2AsBr$$

Extension of this reaction to the preparation of vinylbromostibines and vinylbromophosphines has not led to pure products thus far, and further studies are in progress. In the reaction between di-*n*-butyldivinyltin and bismuth trichloride the experimental method applied to the preparation of the vinylmercuric halides[9b] was used. Vinylbismuth dichloride came out of solution but decomposed rapidly.

Experimental[18]

Vinylation of Phosphorus, Arsenic, Antimony and Bismuth Trihalides.—As an example of the procedure followed in the preparation of Group V trivinyl compounds other than trivinylphosphine, that for trivinylarsine is given.

To 1.5 moles of vinylmagnesium bromide in 500 ml. of tetrahydrofuran (distilled from lithium aluminum hydride prior to use) was added slowly with stirring under an atmosphere of prepurified nitrogen 70 g. (0.387 mole) of arsenic trichloride dissolved in 200 ml. of tetrahydrofuran. After the addition was completed, another 300 cc. of tetrahydrofuran was added and the reaction mixture was refluxed for one hour, then was cooled to room temperature and hydrolyzed with 150 ml. of saturated ammonium chloride solution. The salts subsequently were removed by filtration through a sintered-glass funnel under nitrogen. The filtrate was fractionally distilled using a vacuum-jacketed Vigreux column. After removal of the solvent, distillation was continued under reduced pressure to give 37.4 g. of trivinylarsine, b.p. 45–46° at 41 mm. This represents a yield of 62%.

For the preparation of trivinylphosphine two dropping funnels were used so that a solution of phosphorus trichloride in diethyl ether and a solution of the vinyl Grignard reagent in tetrahydrofuran could be added slowly *and simultaneously* to the flask containing 300 ml. of diethyl ether, stirred and cooled to $-20°$. Upon completion of the addition the reaction mixture was refluxed for six hours, then was cooled and filtered. The solvent was removed at atmospheric pressure until the pot temperature reached 112°. Vacuum was then applied and the distillation continued. Redistillation at atmospheric pressure of the distillate obtained at reduced pressure gave pure trivinylphosphine in low yield. In other experiments it was found that inclusion of a hydrolysis step in the preparation of trivinylphosphine resulted in an even lower yield of the desired compound.

Experimental results for other preparations of the trivinyl compounds are summarized in Table II. During these experiments small quantities of liquids much less volatile than the trivinyl compounds were isolated, but not studied. It should be emphasized that all operations were carried out in an atmosphere of pure nitrogen.

TABLE II

PREPARATION OF TRIVINYL DERIVATIVES OF GROUP V ELEMENTS

Halide (moles)	$CH_2{:}CHMgBr$ (moles)	Yield of $(CH_2{:}CH)_3M^V$	Carbon, %		Hydrogen, %	
			Calcd.	Found	Calcd.	Found
PCl_3, 0.3	1.5	18%	64.27	64.54	8.09	8.26[a]
				64.11		8.36
$AsCl_3$, .3	1.5	62	46.18	46.12	5.81	5.98
$SbCl_3$, .3	1.5	66	35.52	35.36	4.47	4.70
$BiCl_3$, .3	1.5	23	24.84	24.57	3.12	3.13
				24.77		3.15

[a] % P, calcd., 27.64; found, 27.64.

Phenyldivinylphosphine.—To a vinylmagnesium bromide solution prepared from 160 g. (1.5 moles) of vinyl bromide and 36.5 g. (1.5 g. atom) of magnesium turnings in 500 ml. of THF was added 71.6 g. (0.4 mole) of $C_6H_5PCl_2$ dissolved in 200 ml. of tetrahydrofuran. After a reflux period of one hour, the reaction mixture was hydrolyzed with a saturated solution of ammonium chloride. Distillation of the organic layer gave about 4 g. of phenyldivinylphosphine, b.p. 55° at 0.5 mm., a viscous, yellow liquid.

Anal. Calcd. for $C_{10}H_{11}P$: C, 74.06; H, 6.84. Found: C, 74.25; H, 7.19.

In addition, another small fraction boiling 62–64° at 0.5 mm. was obtained. This solidified at room temperature to a colorless, crystalline mass. m.p. 40–45°. Attempts at identification were unsuccessful.

Vapor Pressures of the Trivinyl Compounds of P, As, Sb and Bi.—Representative vapor tensions of the trivinyl derivatives were determined with a tensimeter[19] and are given in Table III. These values led to equations of the form $\log_{10} p(\text{mm.}) = B - A/T$, from which it was possible to calculate the normal boiling points, molar heats of vaporization and Trouton constants listed in Table I.

As can be seen from the data in Table I, trivinylbismuth has a relatively high Trouton constant and a normal boiling point only 8° above that of trivinylstibine. This observation prompted us to examine the difference in boiling points of triethylbismuth and triethylstibine. Since the normal boiling point of triethylbismuth had not been recorded previously, the variation of vapor tension with temperature was determined. Representative values given in Table IV determine the equation $\log_{10} p(\text{mm.}) = 7.952 - 2293/T$, implying a normal boiling point of 178.9° and a Trouton constant of 23.2 cal./degree mole.

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TABLE III

VAPOR TENSIONS OF TRIVINYL DERIVATIVES OF THE GROUP VB ELEMENTS

t, °C.	$p_{mm.}$ (obsd.)	$p_{mm.}$ (calcd.)	t, °C.	$p_{mm.}$ (obsd.)	$p_{mm.}$ (calcd.)
(a) Trivinylphosphine					
16.2	20.4	20.3	40.1	58.9	59.2
21.2	25.7	25.7	44.9	71.4	72.0
26.5	32.7	32.9	49.9	88.0	87.7
35.0	47.9	47.8	54.9	106.3	106.2
			60.9	133.3	132.6
(b) Trivinylarsine					
22.7	16.4	16.3	43.9	42.7	43.0
25.0	18.3	18.3	49.9	54.6	55.2
31.5	24.5	24.8	53.6	64.2	64.1
39.0	34.5	34.8	63.0	92.5	92.4
			65.9	103.1	103.0
(c) Trivinylstibine					
20.2	6.1	6.0	50.5	26.2	26.3
23.9	7.4	7.3	55.0	31.7	32.0
30.0	9.8	10.0	59.8	39.4	39.2
35.0	12.7	12.8	65.0	49.1	48.6
39.9	15.9	16.2	70.0	59.8	59.4
45.1	20.2	20.6			
(d) Trivinylbismuth					
19.9	1.4	1.4	63.0	17.5	17.4
39.4	4.9	4.8	66.0	20.2	20.3
53.0	10.4	10.3	70.0	24.5	24.7
56.5	12.6	12.4	73.5	29.0	29.3
59.9	15.1	14.9			

TABLE IV

VAPOR TENSIONS OF TRIETHYLBISMUTH

t, °C.	28.0	39.9	45.4	53.1	56.0	60.9	64.3	67.4	69.9
$p_{mm.}$ (obsd.)	2.1	4.3	5.6	8.2	9.6	12.1	14.4	16.7	18.8
$p_{mm.}$ (calcd.)	2.2	4.3	5.7	8.4	9.7	12.3	14.4	16.6	18.6

Since the boiling point of triethylstibine is 158.5°, for both ethyl and vinyl substituents the boiling point increment in passing from antimony to bismuth is small, considered in terms of the large increase in molecular weight.

Addition Reactions of the Trivinyl Derivatives of P, As, Sb and Bi with Methyl Iodide, Ethyl Iodide or Vinyl Bromide. (a) **Trivinylphosphine.**—To a tube containing Vi_3P at −78° was added an excess of methyl iodide. The tube was sealed under nitrogen and allowed to warm to room temperature. A vigorous reaction ensued and a white crystalline solid formed. The mixture was left to stand at room temperature for two days. It was then filtered, giving a quantitative yield of $(Vi_3MeP)I$. Pure material was obtained by precipitating it from an alcoholic solution by addition of diethyl ether. A similar procedure was used to prepare $(Vi_3EtP)I$. The yellowish-red adduct Vi_4PBr slowly separated from a mixture of vinyl bromide and trivinylphosphine sealed in a tube under vacuum. The tube was kept in the dark to avoid polymerization of vinyl bromide.

(b) **Trivinylarsine.**—The method described for the preparation of the methyl iodide adduct of trivinylphosphine was used. Reaction in the case of trivinylarsine was much less rapid. Both the methyl iodide and ethyl iodide adducts were purified by precipitating them from solutions in methanol by addition of diethyl ether. No adduct formed, even at 100°, when trivinylarsine and vinyl bromide were mixed and kept in a sealed tube for extended periods of time.

(c) **Trivinylstibine.**—$(Vi_3MeSb)I$ formed from trivinylstibine and an excess of methyl iodide, kept at room temperature in a sealed tube for 65 hr. The white crystalline solid was recrystallized from absolute ethanol. No reaction occurred between trivinylstibine and ethyl iodide or vinyl bromide.

Analytical data and decomposition temperatures for the addition compounds are given in Table V.

(d) **Thermal Decomposition of Vi_3MeSbI.**—Thermal decomposition at reduced pressure of 18.5 g. (0.0538 mole) of Vi_3MeSbI gave CH_3I (identified by its infrared absorption spectrum) and 8.7 g. of Vi_3Sb, b.p. 53° at 32 mm., a yield of 79.5%.

Other Addition Compounds of the Trivinyl Derivatives of P, As and Sb. (a) **Trivinylarsonium Chloride.**—A solution of trivinylarsine in ether was cooled to −20° and anhydrous HCl gas was bubbled through for two hr. Removal of the ether at reduced pressure left a waxy solid, which was subsequently dissolved in absolute ethanol. Filtration, followed by addition of ether, precipitated very hygroscopic, white crystals of the arsonium salt.

Anal. Calcd. for $C_6H_{10}ClAs$: C, 37.43; H, 5.23; Cl, 18.42. Found: C, 37.26; H, 5.50; Cl, 18.14.

(b) **Trivinylphosphine–Boron Trifluoride.**—An 84.7-cc.[20] sample of Vi_3P was treated in a tensimeter[19] with 96.2 cc. of BF_3. A vigorous reaction took place at −78°, a white solid being formed. Subsequently 10.64 cc. of BF_3 was recovered. The ratio of reactants was thus 1:1.01, corresponding to formation of the adduct $Vi_3P{\cdot}BF_3$. This adduct had no apparent saturation pressure at room temperature.

(c) **Carbon Disulfide Adduct of Trivinylphosphine.**—A 14.5-cc.[20] sample of Vi_3P was treated at room temperature with 28.6 cc. of CS_2 in a trap attached to the high vacuum system. After about 15 min. the liquid phase turned pink, and later a red solid separated out. The following day the volatile components in the trap were distilled off, but fractionation showed that reaction between CS_2 and Vi_3P was not complete. The mixture was then distilled into another container of small volume, so that the liquid phase would be large, since it was known[21] that while Me_3P and CS_2 react in the liquid phase, reaction in the gas phase is quite slow. As before, a red solid separated out after a few hours from the Vi_3P–CS_2 mixture. The volatile components were again transferred to a clean container and the procedure was repeated until all of the Vi_3P (which may be condensed at −22.5° in the vacuum system) was used up. Recovery of 13.5 cc. of unused CS_2 established the ratio of Vi_3P:CS_2 to be 1:1.04.

(d) **$[Vi_3M^VI_2PtCl_2$ (M: As and Sb). Trivinylarsine.**—An excess of a saturated aqueous solution of K_2PtCl_4 was shaken with trivinylarsine. The resulting precipitate was filtered, washed with ethanol and with ether, and dried *in vacuo* to give pale yellow solid, m.p. 90°. The ether-soluble *trans*-isomer was not isolated.

TABLE V

ADDITION COMPOUNDS $(Vi_3RM^V)X$

Adduct	Dec. temp., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
$[(CH_2:CH)_3P(CH_3)]I$[a]	198–200	33.09	32.88	4.76	4.66
$[(CH_2:CH)_3P(C_2H_5)]I$[b]	327–328	35.73	35.84	5.25	5.38
$(CH_2:CH)_4PBr$[c]	105–140	43.86	43.81	5.52	5.76
$[(CH_2:CH)_3As(CH_3)]I$	154–156	28.21	28.03	4.06	4.06
$[(CH_2:CH)_3As(C_2H_5)]I$	184–185	30.8	30.9	4.52	4.77
$[(CH_2:CH)_3Sb(CH_3)]I$	119–120	24.38	24.53	3.51	3.29

[a] % I, calcd., 49.95; found, 49.90. [b] % I, calcd., 47.2; found, 47.6. [c] % Br, calcd., 36.48; found, 36.80.

Anal. Calcd. for $C_{18}H_{27}Cl_2As_2Pt$: C, 24.92; H, 3.14. Found: C, 24.90; H, 3.42.

Trivinylstibine.—With trivinylstibine the same procedure gave the corresponding antimony compound; yellow solid, m.p. 113–114°, with decomposition.

Anal. Calcd. for $C_{18}H_{27}Cl_2Sb_2Pt$: C, 21.45; H, 2.70. Found: C, 20.31; H, 2.76.

Compounds $Vi_3M^VI_2$ and their Thermal Decomposition. Trivinylstibine.—To 20 g. of Vi_3Sb dissolved in 50 ml. of

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[20] The term "cc." here refers to gas volume at STP.

[21] H. C. Brown and R. H. Harris, THIS JOURNAL, **71**, 2751 (1949).

CCl_4 was added a solution of 25.02 g. of iodine in the same solvent. Decolorization of the iodine was instantaneous and a light yellow solution resulted. Removal of the solvent at reduced pressure yielded a yellow oil, quite pure Vi_3SbI_2.

Anal. Calcd. for $C_6H_9I_2Sb$: C, 15.78; H, 1.98. Found: C, 15.63; H, 2.24.

Thermal decomposition at reduced pressure of Vi_3SbI_2 gave as identifiable products SbI_3, m.p. 165–167°, and a small yield of Vi_2SbI, b.p. 69° at 1.3 mm.

Anal. Calcd. for C_4H_6ISb: C, 15.86; H, 2.0. Found: C, 15.67; H, 1.85.

Trivinylarsine.—The same procedure gave impure Vi_3AsI_2, a brown-red oil insoluble in CCl_4 and ether, but soluble in tetrahydrofuran.

Anal. Calcd. for $C_6H_9I_2As$: C, 17.58; H, 2.21. Found: C, 15.48; H, 2.23.

Thermal decomposition at reduced pressure of this oil gave vinyl iodide (identified by its infrared absorption spectrum), and a low yield of Vi_2AsI, yellow liquid, b.p. 83° at 17 mm.

Anal. Calcd. for C_4H_6IAs: C, 18.77; H, 2.36. Found: C, 18.69; H, 2.52.

A solid residue in the still pot, presumably AsI_3, was not investigated.

Redistribution of the Trivinyl Derivatives of As and Sb with the Corresponding Trihalides. (a) **Vinyldibromoarsine.**—To 32.51 g. of $AsBr_3$ (0.104 mole) was added 8.25 g. (0.053 mole) of Vi_3As. An exothermic reaction ensued. The reaction mixture was refluxed for one-half hr. at about 60° at 15 mm., and was subsequently fractionally distilled giving: (1) 6.9 g. of yellow liquid, boiling from 65° at 20 mm. to 73° at 14 mm., a mixture of Vi_2AsBr and $ViAsBr_2$; (2) 15.4 g. of yellow liquid, b.p. 74–76° at 14 mm.; (3) 10.3 g. of dark yellow liquid, boiling range 79–85° at 14 mm., probably a mixture of $ViAsBr_2$ and $AsBr_3$; (4) a black solid residue. Fraction (2) is the desired $ViAsBr_2$; yield 37.8%.

Anal. Calcd. for $C_2H_3Br_2As$: C, 9.18; H, 1.16; Br, 61.06. Found: C, 9.37; H, 1.23; Br, 60.95.

(b) **Divinylbromoarsine.**—An exothermic reaction resulted on mixing 10.5 g. (0.067 mole) of Vi_3As and 10.57 g. (0.0335 mole) of $AsBr_3$. The mixture was stirred and heated at 130° under nitrogen for 3 hr. Fractional distillation gave: (1) 1.9 g. of unreacted Vi_3As, b.p. 46° at 41 mm., a recovery of 18%; (2) 7.2 g. of yellow liquid; b.p. 59° at 19 mm.; (3) 0.4 g. of liquid boiling from 60° at 20 mm. to 65° at 13 mm.; (4) a black solid residue. Fraction (2) is Vi_2AsBr, representing a yield of 34.2%, based on $AsBr_3$.

Anal. Calcd. for C_4H_6BrAs: C, 23.00; H, 2.90; Br, 38.25. Found: C, 23.13; H, 3.03; Br, 38.37.

(c) **Vi_3As and $AsCl_3$.**—A mixture of 28.8 g. (0.184 mole) of Vi_3As and 70.0 g. (0.387 mole) of $AsCl_3$ was heated at 100° under nitrogen for 5 hr. The originally light yellow reaction mixture became almost black in that time. Fractional distillation yielded: (1) 7 g. of liquid, boiling 56–58° at 40 mm.; (2) 87.6 g. of liquid, b.p. 60–60.5° at 39 mm. Fraction (2) analyzed well for $ViAsCl_2$, the desired product.

Anal. Calcd. for $C_2H_3Cl_2As$: C, 13.9; H, 1.75. Found: C, 13.97; H, 1.87.

However, attempted butylation resulted not only in the expected n-Bu_2AsVi, but also in n-Bu_3As and n-$BuAsVi_2$, showing that fraction (2) was a mixture.

To a solution of n-C_4H_9MgBr, prepared from 18.24 g. Mg and 102.8 g. of n-BuBr in 200 ml. of diethyl ether, there was added 43.3 g. of fraction (2). A 10-hr. reflux period, followed by hydrolysis with a saturated aqueous solution of ammonium chloride, and fractional distillation of the organic layer gave: (1) n-$BuAsVi_2$, b.p. 56° at 12 mm., 3.6 g.; (2) 0.55 g. of an approximately equimolar mixture of $BuAsVi_2$ and n-Bu_2AsVi, boiling range 56° at 12 mm. to 84° at 10 mm.; (3) n-Bu_2AsVi, b.p. 52–53° at 1.5 mm. or 85–86° at 10 mm., 9.9 g.; and (4) n-Bu_3As, b.p. 76° at 1.2 mm. or 95° at 4.5 mm., 5.03 g.

Anal. for fract. (1): Calcd. for $C_8H_{15}As$: C, 51.62; H, 8.12. Found: C, 52.37; H, 8.62.

Anal. for fract. (3): Calcd. for $C_{10}H_{21}As$: C, 55.55; H, 9.79. Found: C, 55.47; H, 9.58.

Anal. for fract. (4): Calcd. for $C_{12}H_{27}As$: C, 58.53; H, 11,05. Found: C, 58.28; H, 11.01.

Using the yields obtained in this butylation experiment it was calculated that fraction (2) of the Vi_3As-$AsCl_3$ redistribution reaction comprised 24.42% $AsCl_3$, 53.03% $ViAsCl_2$ and 22.55% Vi_2AsCl. This composition would, of course, give good agreement with the theoretical analytical values for $ViAsCl_2$.

(d) **Ethyldibromoarsine.**—An exothermic reaction occurred when 8.0 g. (0.0795 mole) of Et_3As and 31.4 g. (0.1 mole) of $AsBr_3$ were mixed. Fractional distillation of the reaction mixture gave 32.5 g. of liquid, b.p. 93.5° at 1.3 mm. Black solid separated from the distillate after it had stood for a short time. Refractionation at atmospheric pressure gave 20.0 g. of pure $EtAsBr_2$, b.p. 200–201°; crude yield 83%; pure yield 51%.

Anal. Calcd. for $C_2H_5Br_2As$: C, 9.1; H, 1.91; Br, 60.59. Found: C, 8.84; H, 1.64; Br, 60.65.

(e) **Vi_3Sb and $SbBr_3$.**—A mixture of 7.6 g. (0.0375 mole) of Vi_3Sb and 27.1 g. (0.075 mole) of $SbBr_3$ reacted exothermally. The liquid reaction mixture was heated for one-half hr. at 65° at 30 mm. A preliminary distillation gave 21 g. of yellow liquid boiling from 38° at 0.7 mm. to 72° at 0.5 mm. Careful fractionation of this liquid yielded: (1) 3.2 g. of yellow liquid, b.p. 42.5° at 0.7 mm.; (2) 6.3 g. boiling 70–72° at 0.6 mm. which crystallized in the receiver to a solid melting *ca.* 65°. Fraction (1) was Vi_2SbBr.

Anal. Calcd. for C_4H_6BrSb: C, 18.78; H, 2.36. Found: C, 18.86; H, 2.59.

Fraction (2) appeared to be a mixture of $ViSbBr_2$ and $SbBr_3$.

Anal. Calcd. for $C_2H_3Br_2Sb$: C, 7.78; H, 0.98. Found: C, 3.49; H, 0.67.

In a similar reaction between 18.0 g. (0.089 mole) of Vi_3Sb and 64.1 g. (0.177 mole) of $SbBr_3$, 40.5 g. of liquid boiling from 79° at 0.8 mm. to 109° at 0.5 mm. was obtained. This product mixture was alkylated with n-BuMgBr using the method described in (c) of this section. Distillation of this reaction mixture gave: (1) 1.2 g., b.p. 73° at 2.5 mm.; (2) 4.6 g., b.p. 90° at 2.5 mm. or 67° at 0.5 mm.; (3) 0.7 g., b.p. 71–72° at 0.5 mm.; (4) 3.9 g., b.p. 76° at 0.5 mm. Fractions (2) and (4) represented pure compounds, n-Bu_2SbVi and n-Bu_3Sb, respectively.

Anal. of fract. (2). Calcd. for $C_{10}H_{21}Sb$: C, 45.66; H, 8.05. Found: C, 45.51; H, 7.88.

Anal. of fract. (4). Calcd. for $C_{12}H_{27}Sb$: C, 49.17; H, 9.29. Found: C, 48.98; H, 9.38.

(f) **Vi_3Sb and $SbCl_3$.**—An exothermic reaction resulted when 21.3 g. (0.01 mole) of Vi_3Sb and 11.96 g. (0.0053 mole) of $SbCl_3$ were mixed. Distillation of the reaction mixture gave a small yield of unreacted Vi_3Sb and a light yellow liquid, b.p. 60° at 4.5 mm., apparently Vi_2SbCl containing a small quantity of $ViSbCl_2$.

Anal. Calcd. for C_4H_6ClSb: C, 22.73; H, 2.86; Cl, 16.4. Found: C, 21.04; H, 3.51; Cl, 20.63.

"Mixed" Redistribution Reactions. (a) **Divinylbromoarsine by Reaction of $AsBr_3$ and n-Bu_2SnVi_2.**[22]—To 28.7 g. (0.1 mole) of n-Bu_2SnVi_2[9a] was added 23.6 g. (0.075 mole) of molten $AsBr_3$. An immediate rise in temperature to 110° was noted. The mixture was heated on the steam-bath in a nitrogen atmosphere for 6 hours. Distillation of the amber reaction mixture gave a small forerun and then 12.7 g. (81%) of light yellow liquid Vi_2AsBr, b.p. 60° at 20 mm. No attempt was made to isolate the organotin products of this reaction.

Anal. Calcd. for C_4H_6BrAs: C, 23.00; H, 2.90; Br, 38.25. Found: C, 23.20; H, 2.82; Br, 38.10.

(b) **Vinyldibromoarsine by Reaction of n-Bu_2SnVi_2 and $AsBr_3$.**[22]—A similar procedure was used in the reaction of 14.4 g. (0.05 mole) of n-Bu_2SnVi_2 with 31.5 g. (0.1 mole) of $AsBr_3$. Distillation gave a 4 g. forerun, b.p. 56° at 14 mm. to 73° at 14 mm., consisting of a mixture of Vi_2AsBr and $ViAsBr_2$, and then 10.4 g. (39.4%) of pure $ViAsBr_2$, b.p. 73–76° at 14 mm.

Anal. Calcd. for $C_2H_3Br_2As$: C, 9.18; H, 1.16; Br, 61.06. Found: C, 8.94; H, 1.02; Br, 61.68.

(c) **n-Bu_2SnVi_2 and $AsCl_3$.**—A mixture of 28.7 g. (0.1 mole) of n-Bu_2SnVi_2 and 18.0 g. (0.1 mole) of $AsCl_3$ was heated on the steam-bath for 3.25 hr. Distillation gave:

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(22) D. Seyferth, Technical Report, Office of Naval Research Contract No. Nonr-1866(13), February, 1957.

(1) 15 g. of liquid, b.p. 60° at 38 mm.; (2) 14 g., b.p. 84° at 0.5 mm., $n^{25}D$ 1.4973, n-$Bu_2ViSnCl$[9a]; (3) 15 g. of solid residue, n-Bu_2SnCl_2. Fraction (1) was shown by analysis to be a mixture of Vi_2AsCl and $ViAsCl_2$.

Anal. Calcd. for C_4H_6ClAs: C, 29.21; H, 3.68; Cl, 21.56. Calcd. for $C_2H_3Cl_2As$: C, 13.90; H, 1.75; Cl, 41.02. Found: C, 23.37; H, 3.01; Cl, 28.45.

(d) **Vi_3Bi and PBr_3.**—To 20 g. of Vi_3Bi, at −30° under nitrogen, was added dropwise 11 g. of PBr_3. A vigorous reaction ensued. The reaction mixture initially turned yellow, but before the addition was completed, strong fuming commenced with simultaneous blackening and solidification of the mixture. Only a button of metallic bismuth could be isolated.

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Coördination Compounds of Uranium with Organic Bases in Aqueous Solution[1]

BY PHILIP S. GENTILE[2] AND LAWERENCE H. TALLEY

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The stoichiometry of complexes present in uranyl-urea, -thiourea and -guanidine systems in aqueous solution has been determined by absorption spectra and Job's method of continuous variation. Only a combining ratio of 1:4 is evident in the uranyl-urea system at pH 3.5. Confirmation was obtained by isolation of the compound $UO_2(NO_3)_2\cdot[CO(NH_2)_2]_4$. In the uranyl-thiourea system, at pH 3.5, a complex having a uranyl/thiourea combining ratio of 1:4 exists. A uranyl-guanidine complex with a 1:1 mole ratio was also found.

In a previous communication[3] the complexes existing in uranyl-urea, -thiourea and -guanidine systems in absolute ethyl alcohol were reported. These systems were reinvestigated in aqueous media because it has been shown[4] that many uranyl complexes which are formed in non-aqueous solvents differ greatly from those formed in water.

Experimental

Materials.—Uranyl nitrate hexahydrate (Baker and Adamson, A.C.S.), urea (American Cyanamid Company), thiourea (Eastman Kodak Company) and guanidine (Eastman Kodak Company) were used without additional purification.

Analysis.—The method of Gertner and Inkovik[5] was used for the determination of urea. The uranium was assayed by ignition to urano-uranic oxide (U_3O_8).

Procedure.—The method of continuous variation[6] was employed using 0.300 M aqueous solutions of uranyl nitrate hexahydrate, urea, thiourea and guanidine which were adjusted to pH 3.5 by the addition of sodium hydroxide. The ion strength, in all cases was adjusted to 0.8 with sodium chloride.

Spectral-transmission curves were obtained using a model DK-2 Beckman spectrophotometer and Corex cells of 10 mm. light path.

Diaquotetraureadioxouranium(VI) Nitrate.—To 100 ml. of an 1.7 M aqueous solution of uranyl nitrate hexahydrate, 51 g. of urea was added with continuous stirring. The resulting solution was permitted to stand for 24 hours, during which time a yellow precipitate was obtained which was filtered and air dried. This extremely water-soluble compound had a melting point range of 74–76°.

Anal. Calcd. for $UO_2(NO_3)_2\cdot[CO(NH_2)_2]_4\cdot 2H_2O$: U, 35.51; N, 20.90; urea, 35.84. Found: U, 35.49; N, 20.83; urea, 35.78.

Tetraureadioxouranium(VI) Nitrate.—The dihydrate was completely dehydrated in an oven at 110° for two hours.

Anal. Calcd. for $UO_2(NO_3)_2\cdot[CO(NH_2)_2]_4$: U, 37.53; N, 22.08; urea, 37.87. Found: U, 37.50; N, 22.01; urea, 37.81.

Results and Discussion

The spectral curves of the uranyl-urea, -thiourea and -guanidine systems were so similar to that of uranyl nitrate solutions that *major* differences in the spectral bands were not detectable between 420 and 600 mμ. Because of the high absorption for the 0.3 M solutions used, the operational range was limited to 450–600 mμ. However, the increase in extinction coefficients was sufficient to determine the complexes present, utilizing two peaks at 464 and 485 mμ as reference points. Since urea, thiourea and guanidine do not absorb in the visible region, the problem was greatly simplified.

For the uranyl-urea system, application of the method of continuous variation resulted in a maximum at 0.2 (Fig. 1) indicating the presence of a single complex with a 1:4 uranyl/urea mole ratio.

This conclusion was strengthened by the isolation of the compound diaquotetraureadioxouranium(VI) nitrate whose subsequent dissolution in appropriate molarities yielded spectral data coincident with the forementioned curve.

It should be noted that similar studies of the same system in alcoholic solutions resulted in the subsequent isolation of a complex (MR_2) with a 1:2 mole ratio.

One can explain the absence of the MR_2 complex in aqueous media on the basis of its instability and dissociation to MR_4 as

$$MR_2 \longrightarrow {}^1/_2MR_4 + {}^1/_2M \qquad (2)$$

where

$$M = UO_2^{++} \quad MR_2 = UO_2[CO(NH_2)_2]_2^{++}$$
$$MR_4 = UO_2[CO(NH_2)_2]_4^{++}$$

The instability of MR_2 in water was experimentally verified by two different methods. In one case, the addition of sufficient urea to MR_2 solutions, to

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[1] This paper is based on work performed for the Atomic Energy Commission by the National Lead Company of Ohio, Cincinnati, Ohio.

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