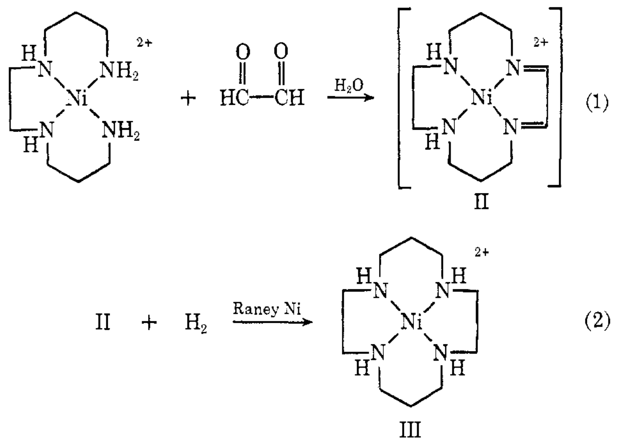

$$\text{III} + \text{excess CN}^- \longrightarrow \text{I} \qquad (3)$$

the connecting organic linkages. The tetramine was first claimed by Van Alphen[1] and was then unambiguously synthesized by Stetter and Mayer[2] by a lengthy process (24% overall yield). Bosnich, *et al.*, used a modification of Van Alphen's procedure for synthesizing the ligand (*ca.* 5% yield) and prepared the first coordination complexes using this tetramine.[3] The present synthesis is a simple one and yields *ca.* 20% of the nickel complex or the free ligand.

Experimental Section

1,5,8,12-Tetraazadodecane, 3,2,3-tet, was prepared by the procedure given by Hamilton and Alexander.[4] The Raney nickel catalyst is Grace Chemical Co. Grade 28.

Preparation of Cyclam.—In a typical preparation (step 1) 26 g (0.15 mol) of 3,2,3-tet and an equivalent amount of $Ni(ClO_4)_2 \cdot 6H_2O$ (54.7 g) were dissolved in 600 ml of water to give a blue solution. The metal–ammine solution was cooled to *ca.* 5° and 24 ml of 40% aqueous glyoxal was added. The solution was stirred well and allowed to stand at room temperature overnight. In step 2 the solution was transferred to a bomb of sufficient volume along with several grams of Raney nickel and hydrogenated under 200–300 psi for 12 hr. In step 3 the catalyst was removed by filtration and 50 g of NaCN was added to the solution which was then heated at reflux for 2 hr. The solution was cooled and then extracted with several 50-ml portions of $CHCl_3$. These extracts were combined, dried with sodium sulfate, and evaporated to dryness. The yellowish solid which resulted was suspended in 100–150 ml of hot acetonitrile for 15–20 min. The suspension was cooled to room temperature and the solid was collected and washed with ether to yield *ca.* 6 g or a 20% yield of cyclam as fine white needles. This material was pure enough for most purposes but the material may be recrystallized from THF or dioxane if desired. *Anal.* Calcd for $C_{10}H_{24}N_4$: C, 59.96; H, 12.07; N, 27.97. Found: C, 59.42; H, 11.78; N, 27.57. The material has infrared and nmr spectra identical with those of cyclam prepared by Tobe's method.[3]

The reaction may be run on a smaller scale and hydrogenated at 50–60 psi using a Parr hydrogenation apparatus, sometimes with a slight reduction in yield.

Isolation of $Ni(cyclam)(ClO_4)_2$.—The nickel complex was isolated after step 2 by evaporation of the filtrate obtained after removal of the catalyst. Orange crystals were obtained after evaporation to *ca.* one-fourth the initial volume. The filtrate was evaporated until it was semisolid and was then taken up in hot water and stirred for a short time with charcoal. The mixture was filtered hot and the filtrate cooled. A second crop of orange crystals was obtained. Evaporation of the filtrate gave a third crop of material. The total yield of dried product was 21% of the theoretical value. All fractions were combined, recrystallized from hot water, and dried *in vacuo*. *Anal.* Calcd for $NiC_{10}H_{24}N_4Cl_2O_8$: C, 26.24; H, 5.29; N, 12.24; Ni, 12.83. Found: C, 26.66; H, 5.10; N, 12.10; Ni, 12.64. *Note!* According to the analyst this material explodes violently upon combustion.

Physical Measurements.—Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer Model 457 spectrophotometer. Nmr spectra were obtained on $CHCl_3$ solutions with a Varian A-60 spectrometer.

Results and Discussion

The reaction scheme utilized in this synthesis involves the well-known condensation of an α-diketone with a primary amine to yield an α-diimine which is stable to hydrolysis as a result of coordination to the metal ion. Such reactions are well known and this method has been used to prepare α-diimine bidentate[5] and tetradentate[6] ligands by condensation of an α-diketo reagent with the appropriate monoamine or diamine, respectively. More recently this method has led to cyclic ligands of the 14-membered type.[7] Much of the earlier work, especially the cyclization reactions, used 2,4-butanedione as the diketo reagent. In the case of cyclization reactions involving a metal template, condensations were successful only in the presence of dilute mineral acid. While conceptually the cyclam synthesis using glyoxal is identical, we were unable to obtain a reaction under these conditions. In aqueous solution, however, glyoxal reacts rapidly with the Ni(II) complex of 3,2,3-tet to yield an intermediate which is presumed to have structure II. Initial efforts to isolate this intermediate have been unsuccessful. Hydrogenation of the intermediate using Raney nickel catalyst yields $Ni(cyclam)^{2+}$ (III in the scheme) which may be isolated if desired. Treating the solution with excess cyanide without isolation of the metal complex leads to free cyclam. It should be noted that the order of addition in the first step is critical. No reaction with the metal ion is apparent even after several days if glyoxal is added to the amine before addition of the nickel salt. Also no cyclam was obtained when 2 equiv of 1,3-diaminopropane was substituted for the tetramine or when the tetramine reacted with glyoxal without addition of nickel ion.

Acknowledgment.—Financial support by the Petroleum Research Fund administered by the American Chemical Society (Grant 2013-G3) and the Graduate College of the University of Illinois (Summer Faculty Fellowship) is gratefully acknowledged.

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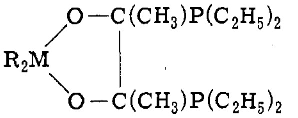
Reactions of Germyl- and Silylphosphines with Glyoxal

BY CLAUDE COURET, JACQUES SATGÉ,* AND FRANÇOISE COURET

Received January 17, 1972

The germyl- and silylphosphines $R_3MP(C_2H_5)_2$ (M = Ge, Si) give a dipolar 1,2 addition on the carbonyl group of aldehydes and of some ketones[1] and on one of the carbonyl groups of diacetyl.[2]

The condensation of bis(diethylphosphino)germanes and -silanes $R_2M[P(C_2H_5)_2]_2$ on diacetyl leads, besides to acyclic 1/1 and 1/2 insertion derivatives, to the 2-sila- or 2-germa-1,3-dioxolanes with phosphorized substituents[2]



Following these first results it seemed interesting to us to study the behavior of these same metal–phosphines with glyoxal.

Experimental Section

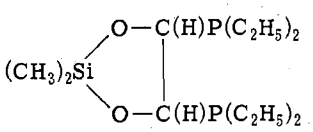
The ir spectra have been performed on a Perkin-Elmer 337 spectrophotometer. The nmr spectra have been recorded on a Varian A-60 spectrophotometer. Tetramethylsilane was used as the internal standard. The chromatographic analyses have been performed on an Aerograph A-90 chromatograph, SE-30 column, on Chromosorb, vector gas helium.

The germylphosphines $(CH_3)_3GeP(C_2H_5)_2$, $(CH_3)_2Ge[P(C_2H_5)_2]_2$, and $(C_2H_5)_2Ge[P(C_2H_5)_2]_2$ have been prepared *via* reaction of $(C_2H_5)_2PLi$ with $(CH_3)_3GeCl$, $(CH_3)_2GeCl_2$, and $(C_2H_5)_2GeCl_2$ according to the method described for the preparation of $(C_2H_5)_3GeP(C_2H_5)_2$.[3] $(C_2H_5)_2Ge(H)P(C_2H_5)_2$ has been prepared *via* the exchange reaction $(CH_3)_3SiP(C_2H_5)_2 + (C_2H_5)_2Ge(H)Cl \rightarrow (CH_3)_3SiCl + (C_2H_5)_2Ge(H)P(C_2H_5)_2$; this rather unstable derivative is used "*in situ.*" The silylphosphines $(CH_3)_3SiP(C_2H_5)_2$, $(CH_3)_2Si[P(C_2H_5)_2]_2$ (I), and $(CH_3)_2Si(H)P(C_2H_5)_2$ have been described by Fritz.[4,5] The anhydrous glyoxal monomer has been prepared according to the method described by Ramirez, *et al.*[6]

Reaction of Glyoxal with Diethyl(trimethylgermyl)phosphine, $(CH_3)_3GeP(C_2H_5)_2$.—The gaseous mixture anhydrous glyoxal monomer–nitrogen bubbled for 5 min in 2.17 g (0.011 mol) of diethyl(trimethylgermyl)phosphine in solution with 5 ml of benzene. The temperature of the reaction mixture rose to 60° with gaseous release. A glc analysis showed the complete disappearance of germylphosphine and the formation of an addition derivative. The reaction mixture was concentrated and then rectified, leading to 1.74 g of a colorless derivative identified to be $(CH_3)_3GeOCH_2P(C_2H_5)_2$ (bp 33° (7.5×10^{-2} mm)) (75% yield). *Anal.* Calcd for $C_8H_{21}GeOP$: C, 40.57; H, 8.94; P, 13.08. Found: C, 40.7; H, 8.9; P, 13.4.

Reaction of Glyoxal with Diethyl(trimethylsilyl)phosphine, $(CH_3)_3SiP(C_2H_5)_2$.—Under the same conditions described previously, glyoxal bubbled for 5 min in 2.01 g (0.012 mol) of diethyl(trimethylsilyl)phosphine in solution with benzene (5 ml). The temperature of the reaction mixture rose quickly to 70° and a gaseous release appeared. The glc analysis showed a complete reaction. After concentration and distillation, 1.69 g of $(CH_3)_3SiOCH_2P(C_2H_5)_2$ was isolated (71% yield) (bp 70° (18 mm)). *Anal.* Calcd for $C_8H_{21}OPSi$: C, 49.96; H, 11.01; P, 16.10. Found: C, 49.7; H, 11.1; P, 15.8.

Reaction of Glyoxal with Dimethylbis(diethylphosphino)silane, $(CH_3)_2Si[P(C_2H_5)_2]_2$.—The gaseous mixture nitrogen–glyoxal bubbled for 5 min in 1.9 g (0.008 mol) of $(CH_3)_2Si[P(C_2H_5)_2]_2$ in benzene solution (10 ml). After concentration and vacuum fractionation 1.18 g of a mixture of compound II and $(CH_3)_2Si[OCH_2P(C_2H_5)_2]_2$ was obtained in relative proportions of 85:15 (bp 75–76° (0.12 mm)) (48% yield).



II

Some very viscous and undistillable polymers remained at the bottom of the distillation apparatus.

Reaction of Glyoxal with Diethylbis(diethylphosphino)germane, $(C_2H_5)_2Ge[P(C_2H_5)_2]_2$.—The germylphosphine $(C_2H_5)_2Ge[P(C_2H_5)_2]_2$ (3.05 g, 0.010 mol) in benzene solution (10 ml) was processed for 10 min by the gaseous mixture nitrogen–glyoxal. The temperature rose to 40°. The concentration and further distillation led to 2.29 g of a colorless derivative identified as $(C_2H_5)_2Ge[OCH_2P(C_2H_5)_2]_2$ (63% yield) (bp 100° (6×10^{-2} mm)). *Anal.* Calcd for $C_{14}H_{34}GeO_2P_2$: C, 45.57; H, 9.29; P, 16.79. Found: C, 45.4; H, 9.2; P, 16.1.

Some undistillable polymers remained at the bottom of the flask.

Reaction of Dichlorodimethylsilane with the Diphospholithium Derivative of Glyoxal.—The lithium compound $(C_2H_5)_2PLi$ was prepared by adding 2.70 g (0.030 mol) of diethylphosphine, $(C_2H_5)_2PH$, in 10 ml of anhydrous THF to 9.50 g of a 20% butyllithium solution in hexane. After 2 hr of refluxing, the lithium compound was processed by a gaseous argon–glyoxal stream. Dichlorodimethylsilane (1.94 g, 0.015 mol) in petroleum ether (20 ml) (bp 45–65°) was then added dropwise to the mixture with mechanical stirring. At the end of the addition, the mixture was centrifuged and the lithium chloride precipitate was eliminated. After concentration and distillation 1.33 g of a colorless compound (II) identical with the derivative already isolated in the addition of glyoxal to $(CH_3)_2Si[P(C_2H_5)_2]_2$ was obtained (30% yield) (bp 78° (0.2 mm)). *Anal.* Calcd for $C_{12}H_{28}O_2P_2Si$: C, 48.96; H, 9.59; P, 21.04. Found: C, 48.5; H, 9.6; P, 20.6.

Some polymers resulting from the intermolecular reactions were formed in the reaction.

Reaction of Dichlorodiethylgermane with the Diphospholithium Derivative of Glyoxal.—$(C_2H_5)_2PCH(OLi)CH(OLi)P(C_2H_5)_2$ was prepared under the same experimental conditions as previously stated from 2.90 g of diethylphosphine (0.032 mol) and 10.31 g of butyllithium. After addition of 3.25 g (0.016 mol) of dichlorodiethylgermane, centrifugation, and concentration, the distillation led to 1.60 g of the derivative $(C_2H_5)_2Ge[OCH_2P(C_2H_5)_2]_2$ (27% yield) (bp 120° (0.8 mm)). This derivative is identical with the compound isolated in the addition of glyoxal into $(C_2H_5)_2Ge[P(C_2H_5)_2]_2$.

Reaction of Glyoxal with Diethyl(hydrodimethylsilyl)phosphine, $(CH_3)_2Si(H)P(C_2H_5)_2$.—The gaseous mixture nitrogen–glyoxal bubbled for 5 min in 1.81 g (0.012 mol) of diethyl(hydrodimethylsilyl)phosphine in benzene solution (5 ml). A strong increase in temperature was noted (70°). Two main fractions were isolated by fractional distillation in relative proportions of 35:65. The first of them was identified with the derivative $(CH_3)_2Si(H)OCH_2P(C_2H_5)_2$ (bp 70° (10 mm)), ir ν(Si–H) 2110 cm^{-1}. *Anal.* Calcd for $C_7H_{19}OPSi$: C, 47.16; H, 10.74; P, 17.37. Found: C, 47.0; H, 10.9; P, 16.8.

The second fraction is identified as II (bp 144° (10 mm)), already isolated in the addition of glyoxal to $(CH_3)_2Si[P(C_2H_5)_2]_2$.

Reaction of Glyoxal with Diethyl(hydrodiethylgermyl)phosphine, $(C_2H_5)_2Ge(H)P(C_2H_5)_2$.—Diethyl(hydrodiethylgermyl)phosphine prepared from 1.43 g (0.009 mol) of diethyl(trimethylsilyl)phosphine, $(CH_3)_3SiP(C_2H_5)_2$, and 1.47 g (0.009 mol) of chlorodiethylgermane, $(C_2H_5)_2GeHCl$, is used "*in situ*" in benzene solution (5 ml). The gaseous mixture nitrogen–glyoxal bubbled into the solution for 10 min. The temperature of the reaction mixture rose to 35°. After concentration and distillation, 1.08 g of the derivative $(C_2H_5)_2Ge[OCH_2P(C_2H_5)_2]_2$ was isolated (67% yield) (bp 100° (6×10^{-2} mm)). This addition compound was identical with that formed in the action of glyoxal to $(C_2H_5)_2Ge[P(C_2H_5)_2]_2$. The presence of $(C_2H_5)_2GeH_2$ in the reaction medium has been detected in nmr δ(Ge–H) 3.70×10^{-6} (quintuplet),[7] in ir ν(Ge–H) 2035 cm^{-1},[8] and in gas chromatography.

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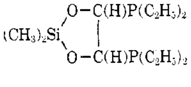
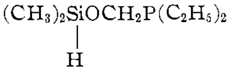
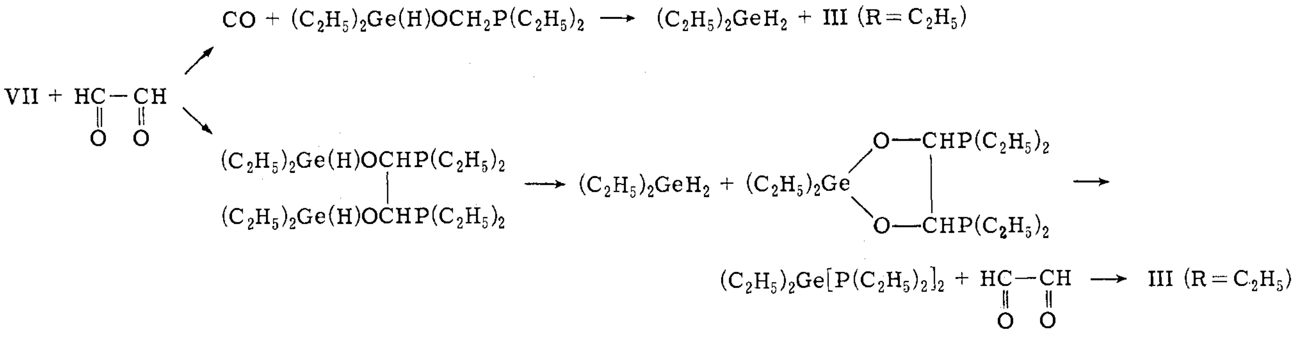
TABLE I

COMPARISON OF SILICON AND GERMANIUM DERIVATIVES[a]

	Nmr data (solvent CD_3COCD_3, int std TMS)	
Compd	δ, ppm	J, Hz
$(CH_3)_3GeOCH_2P(C_2H_5)_2$	$\delta((CH_3)_3Ge)^b$ 0.25 (s; 9 H)	
	$\delta(OCH_2)$ 3.83 (d; 2 H)	$J_{CH_2-P} = 7$
$(CH_3)_3SiOCH_2P(C_2H_5)_2$	$\delta((CH_3)_3Si)$ 0.10 (s; 9 H)	
	$\delta(O-CH_2)$ 3.87 (d; 2 H)	$J_{CH_2-P} = 6.75$
$(CH_3)_2Si[OCH_2P(C_2H_5)_2]_2$	$\delta((CH_3)_2Si)$ 0.25 (s; 6 H)	
	$\delta(O-CH_2)$ 3.97 (d; 4 H)	$J_{CH_2-P} = 6.5$
	$\delta((CH_3)_2Si)$ 0.21 (s; 6 H)	
	$\delta(O-CH)$ 4.19 (d, d; 2 H)	$J_{CH-P} \leq 0.5$ $J_{CH-CH} = 8.5$ $J_{CH-C-P} = 8.5$
 $(CH_3)_2\underset{\displaystyle H}{\underset{\vert}{Si}}OCH_2P(C_2H_5)_2$	$\delta((CH_3)_2Si)$ 0.20 (d; 6 H)	$J_{CH_3-Si-H} = 2.5$
	$\delta(O-CH_2)$ 3.94 (d; 2 H)	$J_{CH_2-P} = 7$
	$\delta(Si-H)$ 4.72 (sept, d; 1 H)	$J_{H-Si-P} = 0.5$
$(CH_3)_2Ge[OCH_2P(C_2H_5)_2]_2$	$\delta((CH_3)_2Ge)$ 0.48 (s; 6 H)	
	$\delta(O-CH_2)$ 3.92 (d; 4 H)	$J_{CH_2-P} = 7$
$(C_2H_5)_2Ge[OCH_2P(C_2H_5)_2]_2$	$\delta(O-CH_2)^b$ 3.75 (d; 4 H)	$J_{CH_2-P} = 7$

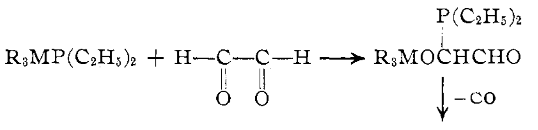
[a] Abbreviations: s, singlet; d, doublet; sept, septuplet. [b] Solvent C_6H_6.

SCHEME I



Results and Discussion

The germyl- and silylphosphines $R_3MP(C_2H_5)_2$ add readily to one of the carbonyl groups of glyoxal. The phosphorized germoxy or siloxy aldehydes which are thus formed are unstable and decarbonylate quickly leading to derivatives which are identical with those which are obtained by addition of formaldehyde to the Ge–P or Si–P bonds



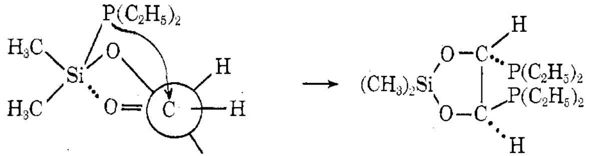
$$R_3MP(C_2H_5)_2 + H-\underset{\displaystyle O}{\underset{\|}{C}}-\underset{\displaystyle O}{\underset{\|}{C}}-H \longrightarrow R_3MO\overset{\displaystyle P(C_2H_5)_2}{\overset{\vert}{C}}HCHO$$

$$\big\downarrow -CO$$

$$R_3MP(C_2H_5)_2 + HCHO \longrightarrow R_3MOCH_2P(C_2H_5)_2$$

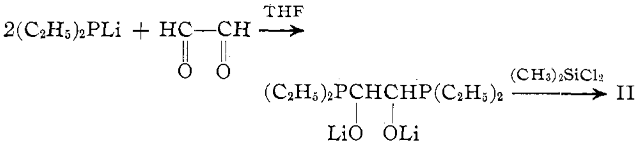
In the action of $(CH_3)_2Si[P(C_2H_5)_2]_2$ (I) on glyoxal, the formation of the cyclic derivative II (45% yield) is observed besides the decarbonylated diaddition derivative $(CH_3)_2Si[OCH_2P(C_2H_5)_2]_2$ (8% yield).

The good yield in siladioxolane can be explained by the easy addition of the metal phosphines to the aldehyde group which gives way to the quick cyclization of the acyclic monoaddition derivative transiently formed. In this cyclization, the asymmetric induction of the first carbon chiral at the time of the concerted addition on the second carbonyl group leads to a very stereoselective reaction with formation of 2-sila-1,3-dioxolane (II) of trans-threo configuration [$\delta(CH_3)_2Si$ 0.21 ppm (singlet)]. The stereospecificity of this reaction is equal at least to 95% (precision limit of nmr).



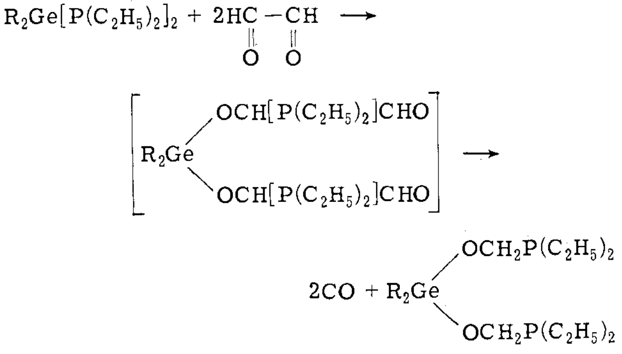
II

II could be obtained *via* the action of dichlorodimethylsilane on the diphospholithium glyoxal derivative



$$2(C_2H_5)_2PLi + H\underset{\displaystyle O}{\underset{\|}{C}}-\underset{\displaystyle O}{\underset{\|}{C}}H \xrightarrow{THF} (C_2H_5)_2P\underset{\displaystyle LiO}{\underset{\vert}{C}}H\underset{\displaystyle OLi}{\underset{\vert}{C}}HP(C_2H_5)_2 \xrightarrow{(CH_3)_2SiCl_2} II$$

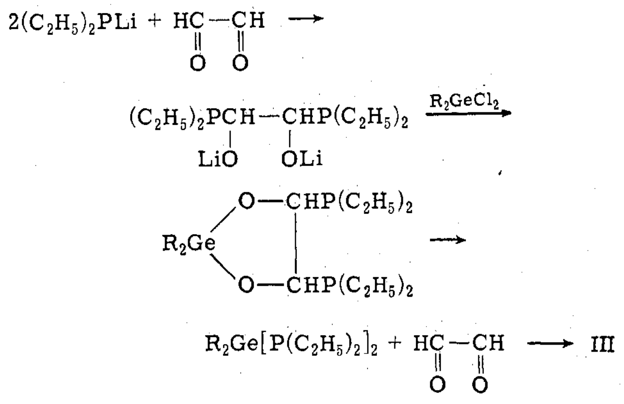
In the action of $R_2Ge[P(C_2H_5)_2]_2$ (R = CH_3, C_2H_5) on glyoxal, the isolog germanium derivative, very unstable, could never be characterized and only $R_2Ge[OCH_2P(C_2H_5)_2]_2$ (III) has been isolated



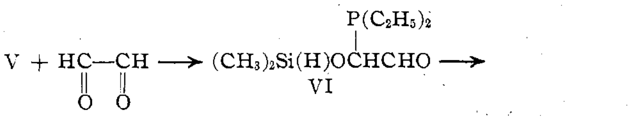
$$R_2Ge[P(C_2H_5)_2]_2 + 2H\underset{\displaystyle O}{\underset{\|}{C}}-\underset{\displaystyle O}{\underset{\|}{C}}H \longrightarrow \left[R_2Ge\begin{array}{l}\diagup OCH[P(C_2H_5)_2]CHO\\ \diagdown OCH[P(C_2H_5)_2]CHO\end{array}\right] \longrightarrow 2CO + R_2Ge\begin{array}{l}\diagup OCH_2P(C_2H_5)_2\\ \diagdown OCH_2P(C_2H_5)_2\end{array}$$

III

However, 2-germa-1,3-dioxolane must form transiently in the course of this reversible addition reaction as in the direct action of a dichlorodialkylgermane on the glyoxal diphospholithium derivative. In this latter reaction also, only III is isolated

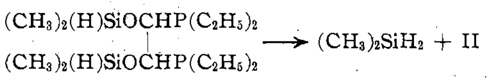


The condensation of diethyl(hydrodimethylsilyl)phosphine, $(CH_3)_2Si(H)P(C_2H_5)_2$ (V), leads to the monoinsertion derivative which decarbonylates quickly



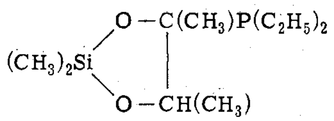
$$\mathrm{V} + \underset{\mathrm{O}\quad\mathrm{O}}{\mathrm{HC{-}CH}} \longrightarrow \underset{\mathrm{VI}}{(\mathrm{CH_3})_2\mathrm{Si(H)O}\overset{\mathrm{P(C_2H_5)_2}}{\mathrm{C}}\mathrm{HCHO}} \longrightarrow \mathrm{CO} + (\mathrm{CH_3})_2\mathrm{Si(H)OCH_2P(C_2H_5)_2}$$

and to the diinsertion derivative which undergoes redistribution into dimethylsilane and the *trans-threo*-2-sila-1,3-dioxolane II already isolated



$$\begin{array}{l}(\mathrm{CH_3})_2(\mathrm{H})\mathrm{SiOCHP(C_2H_5)_2}\\ (\mathrm{CH_3})_2(\mathrm{H})\mathrm{SiOCHP(C_2H_5)_2}\end{array} \longrightarrow (\mathrm{CH_3})_2\mathrm{SiH_2} + \mathrm{II}$$

The instability of the monoinsertion derivative VI has not allowed the intramolecular cyclization by Si–H to carbonyl addition which is observed in the case of diacetyl[2] with formation of the dioxolane



The same reaction studied from the hydrogermylphosphine $(C_2H_5)_2Ge(H)P(C_2H_5)_2$ (VII) has not allowed isolation of the corresponding unstable germanium derivatives. This reaction leads exclusively to the diethylgermane and bis(diethylphosphinomethoxy)diethylgermane, probably according to Scheme I.

The higher thermodynamic stability of the silicon derivatives in comparison with the germanium derivatives can be attributed to stronger silicon–oxygen bond energy than germanium–oxygen[9] and to strong stabilization of the Si–O bond by pπ–dπ effects.[10]

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(9) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworths, London, 1958.

(10) E. A. V. Ebsworth, "Organometallic Compounds of the Group IV Elements," Vol. 1, Part 1, A. G. MacDiarmid, Ed., Marcel Dekker, Inc., New York, N. Y., 1968, Chapter 1.

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Reaction of *trans*-Diazidobis(ethylenediamine)iridium(III) Cation with Acid. Synthesis of *trans*-Bis(chloramine)bis(ethylenediamine)iridium(III) and *trans*-Diamminebis(ethylenediamine)iridium(III) Salts

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Received January 24, 1972

The intial report[1] that *trans*-$[Ir(en)_2(N_3)_2]^+$ reacts with concentrated hydrochloric acid to yield 2 mol of nitrogen indicated the discovery of a new type of reaction. However, the fate of the iridium in this reaction was not determined. As a result of other studies[2,3] on such reactions, it has now been possible to return to the original system and establish that the iridium complex formed is *trans*-$[Ir(en)_2(NH_2Cl)_2]^{3+}$. This paper also reports the synthesis of salts of the new complex *trans*-$[Ir(en)_2(NH_3)_2]^{3+}$.

Experimental Section

Materials.—Iridium trichloride was a loan from the Matthey Bishop Co. Other chemicals were readily available commercially and were used without further purification.

Potassium Hexachloroiridate(IV), K_2IrCl_6.—This starting material was prepared from commercal iridium trichloride by boiling it in aqua regia for several hours, reducing the volume to near dryness, repeating this procedure several times with concentrated hydrochloric acid to remove all oxides of nitrogen, and finally precipitating from hydrochloric acid solution with potassium chloride. The black microcrystals were washed with water and methanol and air-dried. Yields are 60–80%.

***trans*-Dichlorobis(ethylenediamine)iridium(III) Perchlorate, $[Ir(en)_2Cl_2]ClO_4$.**—This complex was prepared by a modification of the literature method.[1] Potassium hexachloroiridate(IV) (12.8 g) was suspended in 75 ml of water at 80° and reduced by the slow addition of 2.85 g (slight excess) of $K_2C_2O_4 \cdot H_2O$. The solution was boiled for 10 min to remove all CO_2 and filtered to remove any unreacted solid.[4] The filtrate was boiled for 20 min with 13 g of ethylenediamine dihydrochloride and 0.1 g of sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$). Concentrated hydrochloric acid (15 ml) was added and the solution was allowed to stand at room temperature for a few hours. The resulting green-brown precipitate was collected by suction filtration. This precipitate was then suspended in 60 ml of hot water and 5 ml of neat ethylenediamine was added to dissolve the solid. The solution was boiled for 10 min, 5 ml of ethylenediamine was added, and the solution was boiled for 1 hr more, the volume being reduced to 30 ml. Enough 12 *M* HCl was added to neutralize the solution (to alkacid test paper) and 1 ml of excess acid was added, lowering the pH to below 2. This solution was boiled for 30 min, the volume being reduced to 30 ml once again. The solution was cooled at 0° for 3 hr and the ethylenediamine dihydrochloride formed was removed by filtration. The resulting filtrate was treated with 7 ml of concentrated $HClO_4$. After 20 min the yellow crystals formed were collected by filtration, washed with methanol and ether, and air dried. Yields varied from 20 to 30%. The product was identified by its reported ultraviolet spectrum.[1] Yields can be increased somewhat by allowing the filtrate from the green-brown precipitate formed in the first step to stand for several days at room temperature and treating the resulting precipitate in the same way.

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(1) R. A. Bauer and F. Basolo, *Inorg. Chem.*, **8**, 2231 (1969).

(2) L. A. P. Kane-McGuire, P. S. Sheridan, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **92**, 5865 (1970).

(3) B. C. Lane, J. W. McDonald, F. Basolo, and R. G. Pearson, *ibid.*, **94**, 3786 (1972).

(4) All filtrations up to this point were made using filter paper, as fine black precipitates formed in these steps will ruin glass frits.