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REACTIONS OF TRIPHENYLSILICON, -GERMANIUM AND -TIN AZIDES WITH THEIR CORRESPONDING HYDRIDES

TSU-TZU TSAI, W. L. LEHN AND C. J. MARSHALL, JR.
Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433 (U.S.A.)

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SUMMARY

The azides of triphenyl-silicon, -germanium and -tin react with their corresponding hydrides to yield $Ph_3SiNHSiPh_3$, $Ph_3SiNHGePh_3$, $Ph_3GeNHGePh_3$, Ph_3SiNH_2, NH_3 and N_2 respectively. The failure to isolate compounds containing tin–nitrogen bonds is attributed to a secondary reaction in which the tin–nitrogen bond is cleaved by the hydride under the reaction conditions.

The reactions of organometallic azides listed in Thayer's review article[1] are thermal and photolytic decomposition, reactions with phosphines, formation of complexes, hydrolysis and addition to olefins. In this note we report the reactions of triphenylsilicon, -germanium and -tin azides with their corresponding hydrides. The general equation for these reactions is shown below:

$$\underset{\text{(I)}}{Ph_3M\text{–}N{=}N{=}N} + \underset{\text{(II)}}{Ph_3M'\text{–}H} \rightarrow Ph_3M\text{–}NH\text{–}M'Ph_3 + N_2$$

where M and M′ are Si, Ge, or Sn and may be the same or different.

All nine possible combinations of the various reactants have been investigated and the results are shown in Table 1. In addition, the following observations were also made.

The temperature necessary to effect reaction varied with the hydride and

TABLE 1

REACTIONS OF GROUP IV AZIDES WITH GROUP IV HYDRIDES

Azide	Hydride	Temp.	Products and yields
Ph_3SiN_3	Ph_3SiH	240°	$Ph_3Si\text{–}NH\text{–}SiPh_3$ (58.5%) + N_2
	Ph_3GeH	200°	$Ph_3Si\text{–}NH\text{–}GePh_3$ (79.6%) + N_2
	Ph_3SnH	100°	$Ph_3Si\text{–}NH_2$ (31%) + Ph_6Sn_2 + N_2
Ph_3GeN_3	Ph_3SiH	200–300°	$Ph_3Si\text{–}NH\text{–}GePh_3$ (11.0%) + N_2
	Ph_3GeH	240°	$Ph_3Ge\text{–}NH\text{–}GePh_3$ (80.0%) + N_2
	Ph_3SnH	100°	$Ph_3Ge\text{–}NH\text{–}GePh_3$ (52.0%) + Ph_6Sn_2 (78%) + N_2
Ph_3SnN_3	Ph_3SiH	180°	No amine products
	Ph_3GeH	230°	$Ph_3Ge\text{–}NH\text{–}GePh_3$ (small amount) + N_2
	Ph_3SnH	100°	NH_3 (70%) + Ph_6Sn_2 (97.0%) + N_2

decreased on going from silicon to germanium to tin. This decrease corresponds to the increase in reactivity of the hydride and is in agreement with the work of Anderson[2-4] who reported an increase in the order of reactivity of the triethylmetal hydrides in the reduction of salts of various transition elements when going from silicon to germanium to tin.

The three organometallic azides used can be thermally decomposed[5]. The decomposition temperatures determined during this investigation were approximately 380°, 320° and 200° for triphenylsilicon, -germanium and -tin azide respectively. In some of the reduction reactions the temperatures utilized approached or exceeded the azide decomposition temperatures and the poor results observed indicated that more than one reaction was taking place. This may account for the low yields observed in some reactions. In the reaction of triphenyltin azide and triphenylsilane, only products from the thermal decomposition of the azide were observed.

The expected tin–nitrogen compounds were not isolated. It has been reported[6,7] that the triphenyltin–nitrogen bond can be cleaved by triphenylstannane with the formation of hexaphenylditin and an amine. It was therefore not unexpected that (triphenylsilyl)amine, bis(triphenylgermyl)amine, and ammonia were the amine products isolated from the reductions utilizing triphenylstannane. The initially formed triphenyltin–nitrogen bonds were apparently cleaved in a much faster competing reaction than reduction of further quantities of the azide by the as yet unreacted triphenylstannane.

(Triphenylgermyl)amine is reported[8] to be unstable and readily converted to the secondary amine. Kraus and Wooster have reported that the primary and secondary (triphenylgermyl)amine are converted to the tertiary amine when heated above 200°. In our observations no evidence could be found for the conversion of the secondary to the tertiary amine. Bis(triphenylgermyl)amine can in fact be vacuum distilled without appreciable decomposition. In a recent report[9], bis(triphenylgermyl)amine was the only form of the three amines isolated.

The three secondary organometallic amines, hexaphenyldisilazane, (triphenylsilyl)(triphenylgermyl)amine and bis(triphenylgermyl)amine can easily be distinguished by their infrared spectra in the 2.5 μ–15 μ region. In addition to the absorptions

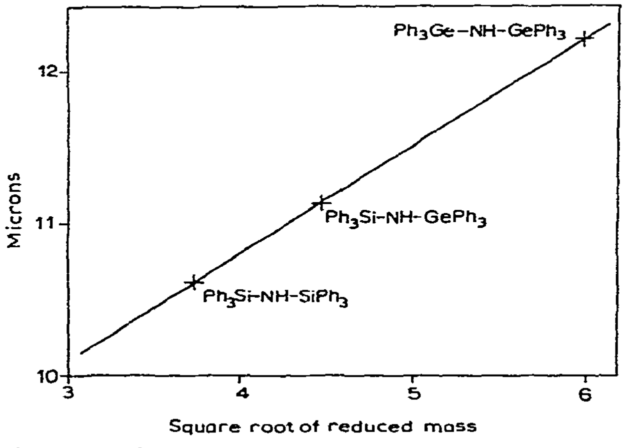

Fig. 1. Plot of wavelength *vs.* square root of reduced mass.

arising from phenyl–metal bonds among which the 7 μ absorption[10] was used as the reference absorption, all three amines have an unshifting absorption at 8.5 μ derived from NH bending vibrations and a shifting asymmetric M–N–M′ stretch vibration. The latter was found to vary with the square root of the reduced mass of the two attached metal atoms (see Fig. 1).

EXPERIMENTAL

Unless otherwise indicated, all melting and boiling points are uncorrected. Infrared spectra were obtained on a Model 137 Perkin Elmer Infracord. Sodium chloride plates were used for solid mulls and liquid films. Potassium bromide pellet techniques were used for most solids.

Unless otherwise indicated, the materials used were reagent grade and were used without further purification.

The triphenyl azide compounds of silicon, germanium and tin were prepared according to the procedures of Thayer and West[11].

Triphenylstannane was prepared according to the procedure used for diphenylstannane[12].

Analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, New York, and Microanalysis, Inc., Wilmington, Delaware.

Molecular weights were determined by mass spectrometry performed by Mellon Institute. Triphenylgermane was obtained from Metallomer Laboratories.

Reaction of triphenylsilicon azide with triphenylsilane

A mixture of 3.0 g (0.01 mole) of triphenylsilicon azide and 2.6 g (0.01 mole) of triphenylsilane was gradually heated under a helium atmosphere. A thermometer with its bulb directly in the reaction mixture was used to measure the temperature. The progress of the reaction (and those that follow) was followed by removing small aliquots and determining their infrared spectra. When the temperature reached 240° a new absorption band at 10.64 μ along with weaker bands at 2.95 μ and a doublet at 8.4 μ and 8.5 μ appeared and increased in intensity with increasing temperature and time. The mixture was heated to a maximum of 320° and held at that temperature for 2 h. The cool reaction mixture was taken up in hot n-hexane. Upon concentration and cooling, a yellow solid, 3.2 g, was obtained, m.p. 165–167°. This material was recrystallized by solution in benzene and dissolution with light petroleum ether (b.p. 30–60°), m.p. 174°, (Lit.[13] for hexaphenyldisilazane, m.p. 175°), yield was 58.5%. (Found: C, 80.63, 80.82; H, 5.69, 5.85; N, 3.05, 2.76; Si, 10.13, 10.22; mol.wt., 533. $C_{36}H_{31}NSi_2$ calcd.: C, 81.05; H, 5.81; N, 2.62; Si, 10.51%; mol.wt., 533.)

In another experiment, identical quantities of reactants were used. After 4 h 0.0078 mole of gas, 2.85 g of hexaphenyldisilazane (m.p. 174°) (yield 52%) and a thick liquid which was tentatively identified by infrared techniques as a mixture of reactants and products were obtained.

Reaction of triphenylsilicon azide with triphenylgermane

A mixture of 3.04 g (0.01 mole) of triphenylgermane and 3.01 g (0.01 mole) of triphenylsilicon azide was heated together. Gas began to evolve rapidly at 200°. In 2 h, 0.0092 mole of gas was collected. The reaction mixture was treated with n-hexane and there was obtained 4.6 g of (triphenylsilyl)triphenylgermylamine, m.p. 161°, yield 78.6%. One crystallization from benzene and petroleum ether (b.p. 30–60°) raised the melting point to 163°. (Found: C, 74.62, 74.85; H, 5.47, 5.24; N, 2.39, 2.63; mol.wt., 575. $C_{36}H_{31}GeNSi$ calcd.: C, 74.76; H, 5.40; N, 2.42%; mol.wt., 575.)

The filtrate upon concentration gave 1.18 g of soft solid. Examination of the infrared spectrum indicated that it was a mixture of reactants and products. It was not investigated further.

Reaction of triphenylsilicon azide with triphenylstannane

A mixture of 3.0 g (0.01 mole) of triphenylsilicon azide and 7.2 g (0.02 mole) of triphenylstannane was heated on a steam bath. The reaction took place immediately and was exothermic, the temperature rose above 100° for a moment. In 15 min, 0.0098 mole of gas was collected. The reaction mixture was treated with petroleum ether (b.p. 30–60°). The solid which was present (2.5 g) was removed by filtration. After recrystallization from benzene and petroleum ether it melted at 224° (Lit.[13] for hexaphenylditin 228–232°). The identity of the hexaphenylditin was confirmed by comparison of its infrared spectrum with that of a known sample and by its reaction with iodine[14].

The petroleum ether filtrate was concentrated and vacuum distilled. At 160° and 0.4 mm, 2.1 g of liquid distilled over. The infrared spectrum of this material indicated that it consisted of triphenylsilylamine[15] and traces of triphenylstannane. One recrystallization, from petroleum ether (b.p. 30–60°) gave 0.84 g of crude (triphenylsilyl)amine, m.p. 54–57° (Lit.[16] m.p. 59°), yield 31%.

Residue remaining in the flask was yellow and weighed 4.1 g. Examination of the infrared spectrum indicated that it consisted of only a phenyl–tin compound, probably hexaphenylditin since it gave a positive reaction with iodine.

Reaction of triphenylgermanium azide with triphenylsilane

A mixture of triphenylgermanium azide (3.6 g, 0.0108 mole) and triphenylsilane (3.0 g, 0.012 mole) was heated at 265° for 6 h. A 55% yield of gas was collected. Workup of the reaction mixture gave 1.3 g of pale brown crystals which by infrared analysis appeared to contain (triphenylsilyl)(triphenylgermyl)amine and hexaphenyldigermoxane as the major components and hexaphenyldisilazane and bis(triphenylgermyl)amine as the minor components. The percentage of (triphenylsilyl)(triphenylgermyl)amine in the mixture was 51% determined by comparing the intensities of the 11.1 μ absorption with those of authentic mixtures and corresponds to a yield of 11.0%.

The remainder of the material appeared to be a mixture of unreacted starting materials plus small amounts of the other products mentioned.

Reaction of triphenylgermanium azide with triphenylgermane

A mixture of 3.5 g (0.01 mole) of triphenylgermanium azide and 3.0 g (0.01 mole) of triphenylgermane was heated at 240° for 4 h. The gas evolved was led first through 50 ml of 0.1012 *N* acid, then collected in a gas buret. There was obtained 0.0071 mole of nitrogen and 0.34 mmole of ammonia. When the syrupy reaction product was treated with n-hexane, a white precipitate formed. There was obtained 5.0 g of crude bis(triphenylgermyl)amine (yield 80.0%). A 1.06-g sample was recrystallized from chloroform and petroleum ether. There was obtained 0.76 g of pure bis(triphenylgermyl)amine, m.p. 159–161° [Lit.[8] for tris(triphenylgermyl)amine 163–174°]. (Found: C, 69.00, 69.18; H, 5.02, 5.05; N, 2.43, 2.42; mol.wt., 620. $C_{36}H_{31}Ge_2N$ calcd.: C, 69.43; H, 4.98; N, 2.25%; mol.wt., 620.)

The bis(triphenylgermyl)amine can be vacuum distilled (0.07 mm, 250°) without appreciable decomposition. The sample thus obtained did not show any change in elemental analysis and molecular weight. (Found: C, 69.06, 69.15; H, 5.19, 4.94; N, 2.51, 2.24%; mol.wt., 620.)

Reaction of triphenylgermanium azide with triphenylstannane

A mixture of 2.4 g (0.007 mole) of triphenylgermanium azide and 4.8 g (0.014 mole) of triphenylstannane was heated on a steam bath. The reaction was evidenced by gas evolution and a rise in temperature of the reaction mixture (max. 143°); 0.008 mole of gas was collected. The reaction mixture was treated with n-hexane. There was obtained 4.5 g of crude hexaphenylditin. One crystallization from chloroform and petroleum ether (b.p. 30–60°) gave 3.8 g (78% yield) of hexaphenylditin which was shown to be 100% pure by iodine titration[14]. From the mother liquid, a wet solid was obtained. Several recrystallizations from chloroform and petroleum ether (b.p. 30–60°) gave 1.1 g of bis(triphenylgermyl)amine, m.p. 152–155° (52% yield). The infrared spectrum of this material was identical to that of an authentic sample. Purification to obtain an analytical sample was not successful.

Attempted reaction of triphenyltin azide with triphenylsilane

A mixture of 3.6 g (0.009 mole) of triphenyltin azide and 2.6 g (0.01 mole) of triphenylsilane was heated under nitrogen. At 180° the mixture turned brown and a solid formed. Heating was continued to 230° and was held at that point for 30 min. After cooling, n-hexane was added and a white solid precipitated, 2.8 g. After one recrystallization from a mixture of chloroform and petroleum ether (b.p. 30–60°), it had a m.p. at 224–226° (Lit.[13] for tetraphenyltin, m.p. 225°). The infrared spectrum was identical to that of tetraphenyltin. It failed to react with iodine solution as did the authentic tetraphenyltin.

The n-hexane filtrate was concentrated. Infrared analysis indicated that the major component was unreacted triphenylsilane.

Reaction of triphenyltin azide with triphenylgermane

A mixture of 3.9 g (0.01 mole) of triphenyltin azide and 3.0 g (0.01 mole) of triphenylgermane was heated at 230° for 2 h. A total of 0.01 mole of gas was collected. The reaction mixture was treated with n-hexane and the insoluble material, 5.2 g, was removed by filtration. The infrared spectrum indicated that this material was a mixture of starting materials plus a phenyltin compound. Upon recrystallization from chloroform, 0.28 g of insoluble material and 1.4 g pure tetraphenyltin was obtained. The tetraphenyltin melted at 223° (Lit.[13] 225°) and failed to react with iodine. The remainder of the material was still a mixture; further attempts to isolate pure materials by recrystallization were not successful.

The hexane filtrate was concentrated and there was obtained 1.7 g of wet solid. Repeated crystallization from chloroform and petroleum ether (b.p. 30–60°) gave a material melting at 154–159°. The infrared spectrum of the material was identical to that of bis(triphenylgermyl)amine. Emission analysis showed that the sample contained Sn 5.2% and Ge 18.2%; calcd. for $Ph_3Ge{-}NH{-}SnPh_3$: Sn, 17.8%, Ge, 10.9%. All absorption in the infrared spectrum could be attributed to the bis(triphenylgermyl)amine. The source of the tin content is apparently from impurities.

Reaction of triphenyltin azide with triphenylstannane

A mixture of 4.0 g (0.01 mole) of triphenyltin azide and 3.5 g (0.01 mole) of triphenylstannane was heated under nitrogen. A vigorous gas evolution was observed when the temperature reached 120°. Infrared analysis of an aliquot of the mixture showed that all of the stannane had reacted and that azide was still present. Further quantities of stannane reacted rapidly with the azide remaining. Upon workup there was obtained 6.4 g of hexaphenylditin and some unreacted triphenyltin azide.

In another experiment, a mixture of 3.9 g (0.01 mole) of triphenyltin azide and 10.5 g (0.03 mole) of triphenylstannane was heated on a steam bath. The evolved gas was led first through 100 ml of 0.1012 *N* HCl, then collected in a gas buret. There was obtained 0.007 mole of ammonia and 0.013 mole of nitrogen. The reaction mixture was treated with n-hexane. The insoluble hexaphenylditin (13.5 g) was removed by filtration; m.p. 225°, yield 97%. Iodine titration[14] indicated that it was 95.5% pure.

Thermal decomposition of triphenylgermanium azide

Triphenylgermanium azide, 1.3 g (0.0038 mole) was heated gradually in a small flask equipped with a condenser and a gas buret. At 200–320° in 4 h, 13 cc of gas were collected. Gas evolution became fast at 320°. The decomposition was complete in 1.5 h (final temperature 345°). Total gas collected was 94 cc (0.0041 mole).

The substance in the flask was a dark brown gum. No identifiable products were isolated.

Thermal decomposition of triphenyltin azide

Triphenyltin azide 1.3 g (0.0033 mole) was heated as above. At 200° gas evolved readily and the reaction was complete in a few minutes, 87 cc (0.0034 mole) was collected.

The black substance in the flask was extracted with boiling chloroform. There was obtained 0.7 g of black crystals. The crystals were taken up again in chloroform and decolorized with charcoal. There was obtained 0.4 g of tetraphenyltin, m.p. 222–227°, mixture m.p. 225–228°. It failed to react with iodine as did the authentic tetraphenyltin.

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