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Preparation, Properties, and Thermal Decomposition Products of Organoazides of Silicon, Germanium, Tin, Lead, Phosphorus, and Sulfur

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The following azides have been prepared and characterized: $(C_6H_5)_3SiN_3$, $(C_6H_5)_2Si(N_3)_2$, $C_6H_5Si(N_3)_3$, $(CH_3)_3SiN_3$, $(CH_3)_2Si(N_3)_2$, $CH_3Si(N_3)_3$, $(C_6H_5)_3GeN_3$, $(C_6H_5)_3SnN_3$, and $(C_6H_5)_3PbN_3$. The surprisingly high stability of these substances is correlated with the degree to which the central atom can $d\pi$–$p\pi$ bond with the p-electrons on the adjacent azide nitrogen. On thermal decomposition triphenylsilyl azide yields up to 60% of the cyclic dimer $[(C_6H_5)_2Si{-}NC_6H_5]_2$, the remainder was the corresponding linear polymer. Triphenylgermanium azide decomposes on heating to yield products having phenyl groups bound to nitrogen. Triphenyltin azide and triphenyllead azide yield nitrogen and the tetraphenyltin and lead compounds. Benzenesulfonyl azide affords azobenzene, nitrogen, sulfur dioxide, as well as unidentifiables, and diphenylphosphinic azide gives products with phenyl groups bound to a nitrogen atom. This is the first observation of a Schmidt-type phenyl group migration from silicon, germanium, phosphorus, and sulfur to adjacent nitrogen.

Introduction

At the beginning of this study of the silyl azides in November, 1961, only silicon tetraazide had been reported.[1] Triphenyllead azide,[2a,b] bis(2,4,6-trimethylbenzene)boron azide,[3] diphenylphosphinic azide,[4,5] benzenesulfonyl azide,[6–9] and diphenylphosphinous azide[10] had also been prepared and their mode of decomposition investigated briefly. A surprising number of notes on the preparation and properties of individual organosilyl azides have appeared this past year[11–19] as well as two articles on organotin azides.[20,21] Additional work on the preparation and thermal decomposition of several of these azides is reported in this paper.

Experimental

The azides were prepared by the following general reaction which has also been used by others in a modified form.

$$MN_3 + R_3SiX \xrightarrow{\text{solvent}} R_3SiN_3 + MX$$

Since the products are very readily hydrolyzed by even traces of moisture, all reagents were carefully dried and an atmosphere of dry argon was used. *These compounds are potentially explosive and toxic. Adequate safety precautions should be observed.* The elemental analyses of the trimethylsilyl azide, dimethylsilyl diazide, and methylsilyl triazide were completely erratic due to the very great ease of hydrolysis of these substances. The only structure proof available is the method of preparation and the infrared spectra. The latter exhibit the intense 2100 cm.$^{-1}$ band and the 1320 cm.$^{-1}$ band characteristic of the Si–N_3 vibrations. The spectra appeared to be free of Si–OH and Si–O–Si vibrations. The infrared spectra of the azides were observed in dilute chloroform solution (1%). The asymmetric stretching vibration of the azide radical was calibrated against the 1946 cm.$^{-1}$ band of polystyrene.

The phosphine imides were prepared by heating stoichiometric quantities of azide and triphenylphosphine until gas evolution stopped. The resulting solid was purified by crystallization. The phosphine imides of the three methylsilyl azides, the triphenyltin azide, and the triphenyllead azide could not be prepared.

Preparation of Azides and Phosphine Imides. Triphenylsilyl Azide.—A sample of 31.1 g. (0.106 mole) of triphenylsilyl chloride and 15.1 g. (0.308 mole) of anhydrous lithium azide in 400 ml. of pyridine was refluxed for 20 hr. The solvent was removed under vacuum, the solid extracted with hot hexane, and the product crystallized twice from hot hexane; 18.7 g. (58% yield); m.p. 83.5–84.5°, lit. 81°,[12] 79–80°[14]; infrared 2034 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{15}N_3Si$: N, 13.95. Found: N, 13.9.

Triphenylsilyltriphenylphosphine imide m.p. 216–217° (from methylene chloride–cyclohexane), lit.[15] 215–216°.

Anal. Calcd. for $C_{36}H_{30}NSiP$: C, 80.74; H, 5.61; N, 2.62; P, 5.79. Found: C, 80.60; H, 5.52; N, 2.53; P, 5.70.

Other Phenylsilyl Azides.—The diphenylsilyl diazide and phenylsilyl triazide were prepared from the respective chlorides by the above procedure. The solvent-free extracts were flash distilled. Diphenylsilyl diazide, 63% yield; b.p. 108–110° (0.03 mm.), lit.[15] 85–90° (10^{-3} mm.).

Anal. Calcd. for $C_{12}H_{10}N_6Si$: C, 54.17; H, 3.76; N, 31.55. Found: C, 53.52; H, 3.53; N, 30.41.

Diphenylsilylbis(triphenylphosphine imide) m.p. 194–195° (from benzene–cyclohexane), lit.[15] 190–191°.

Anal. Calcd. for $C_{48}H_{40}N_2P_2Si$: C, 78.25; H, 5.44; N, 3.81; Si, 3.81. Found: C, 77.90; H, 5.36; N, 4.14; Si, 4.00.

Phenylsilyl triazide, yield undetermined; b.p. 67–71° (0.03 mm.), lit.[18] 62.5–63.5° (0.01 mm.).

Anal. Calcd. for $C_6H_5N_9Si$: C, 31.20; H, 2.16; N, 54.52; Si, 12.12. Found: C, 30.76; H, 2.01; N, 54.02; Si, 12.80.

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Phenylsilyltris(triphenylphosphine imide) m.p. 225–226° (from benzene).

Anal. Calcd. for $C_{60}H_{50}N_3P_3Si$: C, 77.16; H, 5.36. Found: C, 77.37; H, 5.24.

Trimethylsilyl Azide.—A sample of 20.0 g. (0.408 mole) of lithium azide and 41.0 g. (0.376 mole) of trimethylsilyl chloride was brought to reflux in 450 ml. of 2,4-lutidine. Volatiles boiling below 154° were flash distilled and these in turn redistilled through a 90-cm. packed column; 29.9 g. (67% yield); b.p. 96.0–96.2°, lit. 96°,[17] 87°.[13]

Other Methylsilyl Azides.—The dimethylsilyl diazide and the methylsilyl triazide were prepared from the respective chlorides by the above method. The solvent employed was synthetic quinoline. Dimethylsilyl diazide, 20% yield; b.p. 126–130°, lit.[17] 144°. Methylsilyl triazide, 25% yield; b.p. 75–78° (22 mm.), lit.[18] exploded 70° (20 mm.). A concentrated solution of this azide in quinoline evolved gas at 180° and exploded at 190–200° (760 mm.).

Silyl Triazide.—This compound could not be prepared because on gradual addition of 5.8 g. (0.043 mole) of trichlorosilane to a cool (0°) slurry of 10 g. (0.102 mole) of lithium azide in 250 ml. of pyridine, silane was evolved as a colorless gas (passed −78° trap, burns spontaneously in air to SiO_2). This gas is rapidly absorbed by bromine in carbon tetrachloride; silane from 0.043 mole of trichlorosilane consumed 0.0376 mole of bromine, 87% of theory.

Triphenylgermanium Azide.—A sample of 10.7 g. (0.028 mole) of triphenylgermanium bromide was refluxed for 20 hr. with 25 g. (0.387 mole) of finely ground sodium azide in 450 ml. of benzene. One ml. of a saturated ether solution of lithium aluminum hydride was used as a catalyst. Filtration, solvent removal, and three crystallizations from hot hexane gave colorless crystals; 5.0 g. (52% yield); m.p. 107–107.5°; infrared 2007 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{15}N_3Ge$: C, 62.49; H, 4.34; N, 12.15. Found: C, 62.24; H, 4.44; N, 11.87; Br, 0.0.

Triphenylgermanium triphenylphosphine imide m.p. 192–193° (from benzene).

Anal. Calcd. for $C_{36}H_{30}NGeP$: C, 74.51; H, 5.18; N, 2.41. Found: C, 75.31; H, 5.39; N, 2.20.

Triphenyltin Azide.—This compound was prepared from aqueous sodium azide and triphenyltin chloride in ethanol,[20,21] 45% yield; m.p. 111.5–112.5°, lit.[20,21] 115–116°; infrared 2085 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{15}N_3Sn$: C, 55.11, H, 3.83; N, 10.71. Found: C, 55.05; H, 3.96; N, 10.56; Cl, 0.0.

Triphenyllead Azide.—This compound was prepared from aqueous sodium azide and triphenyllead chloride in acetonitrile, 49% yield; m.p. 187.5–188.5°, lit.[2] 186–187°; infrared 2061 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{15}N_3Pb$: C, 45.00; H, 3.12; N, 8.74. Found: C, 44.94; H, 3.09; N, 8.96; Cl, 0.0.

Diphenylphosphinic Azide.—This was used as received from American Potash and Chemical Corporation.

Benzenesulfonyl Azide.—This was prepared from aqueous sodium azide and benzenesulfonyl chloride in ethanol,[7] followed by crystallization from hexane–chloroform (−15°).

Anal. Calcd. for $C_6H_5N_3O_2S$: N, 22.95; S, 17.50. Found: N, 22.72; S, 17.33.

Benzenesulfonyltriphenylphosphine imide m.p. 160–161° (from benzene–cyclohexane).

Anal. Calcd. for $C_{24}H_{30}NO_2PS$; C, 69.11; H, 4.79; N, 3.36; S, 7.66. Found: C, 69.25; H, 4.79; N, 3.28; S, 7.55.

Thermal Decomposition of Azides. Liquid Phase Decomposition of Triphenylsilyl Azide.—Triphenylsilyl azide (4.90 g.) was placed into an argon-flushed test tube and gradually heated from 200° in a metal bath. Gas evolution set in slowly above 350° and became vigorous at 400°. Gas evolution ceased after about 0.5 hr. at 400°. Cooling yielded 4.30 g. (0.46 g. calcd. for loss of N_2) of a brown, brittle solid, m.p. 96–108°.

Anal. Calcd. for $C_{18}H_{15}NSi$: C, 79.14; H, 5.49; Si, 10.25, N, 5.12. Found: C, 78.33; H, 5.46; Si, 10.58; N, 5.44.

This brown solid was dissolved in benzene and chromatographed on a 1 × 45 cm. Woelm alumina (activity one, neutral) column. Elution with 1.2 l. of benzene, evaporation, charcoal treatment, and crystallization (twice) from benzene yielded 0.15 g. of colorless crystals, m.p. 358–359°.

Anal. Found: C, 79.67; H, 5.66; Si, 9.97; N, 4.98.

Further extraction of the column with methylene chloride and ethanol–methylene chloride resulted in no crystalline solids but only an amorphous, brittle solid, m.p. 70–80°.

Anal. Found: C, 78.20; H, 5.54; Si, 11.89; N, 4.10; mol. wt., 657 (ebullioscopic in methyl ethyl ketone).

Vapor Phase Pyrolysis of Triphenylsilyl Azide.—A 2.5 × 45 cm. quartz glass tube was packed to about 25 cm. length with 1-cm. broken Vycor glass chips. The azide (4.0 g.) was placed into one end, and a high capacity vacuum pump was attached to the other end. The packed section of the tube was preheated to 680° (thermocouple measurement inside tube). The section containing the azide was then quickly heated to 100° and the material sublimed into the decomposition zone. The pressure rose to about 0.5 mm. and returned to 0.02 mm. after 17 min. A dark brown, semicrystalline solid had collected at the heater outlet. This material (3.20 g.) contained no azide groups (infrared). Extraction with hot cyclohexane removed most of the color. The insolubles weighed 1.70 g.; 47.2% yield of crude dimer.

With the pyrolysis section temperature at 590° virtually no pyrolysis takes place. At 850° the product is quite badly affected and almost black. Variation of the throughput rate (from 17 min. to 7 hr./4 g. of azide) made little difference in dimer yield. Under the usual pyrolysis conditions (725°) the dimer was recovered unchanged in 90% yield after passage through the hot reactor.

Structure Proof of M.p. 358° Compound. Pyrolysis of Diphenylsilyl Dianilide to M.p. 358° Compound.—A sample of 0.8 g. of diphenylsilyl dianilide (prepared from the diphenylsilyl dichloride and aniline; m.p. 166.5–167.5°, lit.[22] 162°) was quickly heated to 450° in a metal bath and kept there for 10 min. The evolving aniline was pumped off. The residue (0.65 g., 0.60 g. calcd.) was crystallized once from hot chlorobenzene; m.p. 358–359.5°, m.m.p. with purified pyrolysis product undepressed; mol. wt. calcd. 546 (dimer), found 559 (vapor phase osmometer, 100°, chlorobenzene). The infrared spectrum as well as the X-ray powder pattern of the synthetic compound and the azide pyrolysis product were superimposable.

Acid Hydrolysis of M.p. 358° Compound from Triphenylsilyl Azide Pyrolysis.—A sample of 2 g. of m.p. 358° compound was digested for 24 hr. with 75 ml. of ethanol and 10 ml. of concentrated hydrochloric acid. The volatiles were removed and the remaining gums were dissolved in carbon tetrachloride–water and the layers separated. The carbon tetrachloride layer yielded 1.45 g. (1.45 g. of $(C_6H_5)_2SiO$ calcd.) of a brown gum on drying. The infrared showed the typical phenyl, phenyl–Si, Si–O–Si vibrations.

Anal. Calcd. for $C_{12}H_{10}SiO$: C, 72.75; H, 5.05; Si, 14.12. Found: C, 64.68; H, 4.52; Si, 13.15; N, 0.25.

The water layer was treated with 3.70 g. of bromine dissolved in 40 ml. of carbon tetrachloride and the excess bromine and carbon tetrachloride were pulled off under vacuum. The crystalline solid which separated in the water layer was filtered off and dried; 2.20 g., 2.42 g. calcd. for 2,4,6-tribromoaniline; 91% yield; m.p. 122.5–123.5°, lit.[23] 119–120°.

Anal. Calcd. for $C_6H_4NBr_3$: Br, 72.75; N, 4.24. Found: Br, 74.72; N, 4.28.

The melting point was undepressed by authentic 2,4,6-tribromoaniline and the respective infrared spectra were superimposable.

Acid Hydrolysis of Triphenylsilyl Azide Pyrolysis Gums.—The cyclohexane-soluble gums of a triphenylsilyl azide vacuum-

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(22) E. Larsson and L. Bjellerup, *J. Am. Chem. Soc.*, **75**, 995 (1953).

(23) N. A. Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 8th Ed., 1952, p. 682.

flow system pyrolysis (1.55 g.) were hydrolyzed as above. The carbon tetrachloride layer yielded 1.08 g. (96% of theory for $(C_6H_5)_2SiO$) of a brown gum. Bromination of the water layer and work-up yielded 0.75 g. (40% yield) of 2,4,6-tribromoaniline.

Thermal Decomposition of Diphenylsilyl Diazide (Static System).—This diazide (8.80 g., 0.0331 mole) was placed into a test tube and heated from 150° in a metal bath; provision was made to measure the evolved nitrogen. Gas began to evolve at 310–330°; the reaction was carried out largely at 350° (5 hr.); 1550 ml. (STP) of gas was evolved (0.0692 mole, 104.5% of theory). The brown, hard, brittle residue weighed 6.60 g.

Anal. Calcd. for $C_{12}H_{10}N_2Si$: C, 68.58; H, 4.76; N, 13.33; Si, 13.33. Found: C, 69.78; H, 4.73; N, 10.15; Si, 14.70.

Thermal Decomposition of Diphenylsilyl Diazide (Flow System).—Diphenylsilyl diazide (4.40, 0.01655 mole) was slowly distilled through a 30 × 1 cm. pyrolysis tube at 550° and 0.01–0.1 mm. during a 9-hr. period. Immediately after the pyrolysis tube there was a deposit of a brittle brown solid (about 2 g.).

Anal. Calcd. for $C_{12}H_{10}N_2Si$: C, 68.58; H, 4.76; N, 13.33; Si, 13.33. Found: C, 63.75; H, 4.62; N, 11.11; Si, 15.24.

The infrared spectrum of this material was similar to that of the static pyrolysis product. The brominated aqueous layer from an acid hydrolysis yielded a very small quantity of a colorless solid which was not the 2,4-6-tribromoaniline. This product was unidentifiable as were the products in the organic phase of the extraction step.

Thermal Decomposition of Phenylsilyl Triazide.—When phenylsilyl triazide was heated in a test tube in a metal bath it refluxed vigorously at 325° (bath temperature) without gas evolution. The substance was then heated at 400° for 1 hr. in a bomb under 800 p.s.i. nitrogen pressure. On opening it was found that the azide had decomposed. A black charcoal-like substance was present which had very weak phenyl absorptions in its infrared spectrum.

Vapor Phase Pyrolysis of Trimethylsilyl Azide.—The apparatus consisted of an unpacked 30 × 1.5 cm. Vycor tube, a 50-ml. two-necked flask connected to one end of the tube, and a Dry Ice trap on the other end. A slow stream of dry nitrogen was used to push the vapor of 4.90 g. of the azide through the tube heated to 500° during a 3-hr. period. The Dry Ice trap contained 2.5 g. of a liquid which was flash distilled; the distillate had a very wide boiling range: 40° (760 mm.) to 100° (2 mm.).

Anal. Found: C, 39.58; H, 9.64; N, 19.82; Si (by difference), 31.0; ratio C:H:Si:N, 3.0:8.7:1.0:1.3.

A vapor phase chromatographic examination of this material showed that it contained about twenty compounds.

Miscellaneous Reactions.—Triphenylsilyl azide was recovered unchanged after refluxing with one-third mole quantity of aluminum bromide in cyclohexane for 19 hr. This same azide would not react with benzonitrile to yield a tetrazole (200°, 20 hr.). Ultraviolet radiation (2537 Å.) in cyclohexane solution appeared to have produced a partial decomposition,[11,12] but no pure compounds could be isolated. The triphenylsilyl azide did not react with chromium or tungsten hexacarbonyl (200–400°) in an inert atmosphere, with benzene at 350° in a sealed tube (12 hr.), or with anthracene (400°, 1 hr.). In the latter two media only the m.p. 358° dimer and gums could be recovered.

Thermal Decomposition of Triphenylgermanium Azide.—This azide (2.75 g., 0.00795 mole) was pyrolyzed in a test tube. The metal bath temperature was gradually raised from 200 to 400°. At 375° the gas came off slowly; the reaction was held at 400° for 0.5 hr. The gas evolution was 183 ml. (STP, 0.00817 mole of N_2, 103% of theory). The tube contents was a dark brown solid.

Anal. Calcd. for $C_{18}H_{15}NGe$: C, 67.94; H, 4.71; N, 4.40. Found: C, 66.97; H, 4.55; N, 3.05.

Chromatography over Woelm alumina (neutral grade, using benzene and methylene chloride) yielded only gums. Acid hydrolysis of a gas phase pyrolysate (680°) resulted in a 38.5% yield of 2,4,6-tribromoaniline.

Thermal Decomposition of Triphenyltin Azide.—This azide (5.70 g. 0.01455 mole) was heated at 300° in a test tube. The gas evolution was very rapid and ceased after 15 min. (350 ml. STP, 0.01556 mole, 107.3% of theory). The residue was a dark brown, partially crystalline substance with some sublimate.

Anal. Calcd. for $C_{18}H_{15}NSn$: C, 59.33; H, 4.12; N, 3.85; Sn, 32.70. Found: C, 57.61; H, 4.13; N, 2.05; Sn, 27.40.

The residue was subject to sublimation (250° (0.01 mm.)). Of a 0.70 g. charge, 0.45 g. sublimed and was identified as tetraphenyltin (69% yield) by analysis, infrared spectrum, and mixture melting point. The residue (0.25 g.) was a black solid. This was acid hydrolyzed and worked up for 2,4,6-tribromoaniline; 2.1 g. of residue yielded 0.05 g. of a brown solid whose infrared spectrum contained all bands characteristic of this tribromide in addition to several others.

Thermal Decomposition of Triphenyllead Azide.—This azide (3.50 g.) was placed into a 225° metal bath in a test tube. After 2–3 min. a rapid evolution of gas set in which suddenly blew the vent stopper off the test tube. A large, luminous, sooty flame appeared. The tube contents, some black solid and colorless crystals, was extracted with chloroform and filtered, and the solvent-free extract was sublimed twice. This yielded colorless crystals, m.p. 68–69°, which were identical with diphenyl in infrared spectrum and exhibited an undepressed mixture melting point.

A sample (2.10 g.) of this azide was placed into a test tube in a 185° metal bath. The temperature was slowly increased to 220° and kept there for 0.5 hr. Very little gas was given off. The tube contents was then extracted with hot benzene. The extracts yielded 1.35 g. of crystals, 80% of theory, m.p. 222–223°, which were identical in infrared spectrum and undepressed mixture melting point with authentic tetraphenyllead. The residue was a brown powder (0.25 g.).

Vapor Phase Decomposition of Benzenesulfonyl Azide.—At 625° this azide (11.50 g.) was slowly dropped into the vertically mounted, hot 30 × 1.5 cm. Vycor tube over a 4-hr. period (0.5 mm.). The black-brown condensate on the tube exit (outside packed with Dry Ice) weighed 4.5 g. (5.72 g. calcd. for C_6H_5N).

Anal. Calcd. for C_6H_5N: C, 79.11; H, 5.49; N, 15.40. Found: C, 71.08; H, 5.07; S, 2.39; N, 11.67, O (by difference), 9.79; ratio C:H:N:O:S, 6.0:5.2:0.86:0.63:0.08.

This entire product was dissolved in a small amount of warm benzene and chromatographed on a 1 × 25 cm. Woelm alumina column (neutral grade) with benzene, yielding 1.0 g. of red crystals (purified m.p. 68°).

Anal. Calcd. for C_6H_5N: N, 15.40. Found: N, 15.55.

These were identified as azobenzene by infrared spectrum and undepressed mixture melting point. Further elution of the chromatography column with chloroform and chloroform–10% methanol yielded black, amorphous gums.

Anal. Found: C, 73.76; H, 5.19; S, 3.95; N, 8.61; O (by difference), 8.49; ratio: C:H:N:O:S, 6.00:5.0:0.6:0.52:0.12.

No 2,4,6-tribromoaniline could be recovered from an acid hydrolysis of a portion of the gross pyrolysis product.

Pyrolysis of Diphenylphosphinic Azide.—This azide (6.50 g.) was pyrolyzed under vacuum in a Vycor chip packed tube (680°). Passage through the reactor took about 1 hr.; 4.5 g. of a semisolid material was recovered.

Anal. Calcd. for $C_{12}H_{10}PNO$: C, 66.99; H, 4.65; P, 14.42, N, 6.50. Found: C, 66.98; H, 5.08; P, 13.94; N, 5.26.

The aqueous extract of the acid hydrolysate gave an amount of 2,4,6-tribromoaniline equal to 71.6% of theory. No phenylphosphonic acid could be recovered.

Discussion

The unusual stability of these azides, save that of the benzenesulfonyl azide[8,24] (Table I), was very surprising. The stabilization of the silyl azides toward

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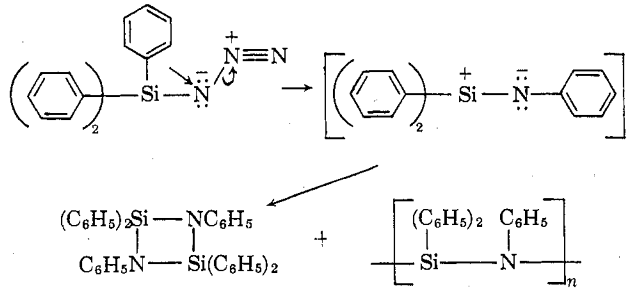
[24] J. Goerdeler and H. Ullmann, *Ber.*, **94**, 1067 (1961).

thermal decomposition is best effected by phenyl groups bound to silicon. Even a single phenyl group yielded a compound of impressive stability: phenylsilyl triazide (54% N_2) decomposed above 325°. The replacement of this phenyl group by a single methyl radical yielded methylsilyl triazide (74% N_2) which was still stable to about 180°. Unfortunately silyl triazide ($HSi(N_3)_3$), if formed in the reaction between silyl trichloride and lithium azide in pyridine (0°), was not stable to disproportionation to silane. Silicon tetraazide, the last in this series, has been found by others[1] to be a highly unstable substance.

The decomposition products of these compounds were of some interest. By analogy with the triphenylmethyl azide rearrangement to benzophenone anil,[25] triphenylsilyl azide expelled nitrogen with rearrangement and the probable monomeric intermediate then polymerized to the corresponding 1,1,2,3,3,4-hexaphenylcyclodisilazane and the poly-1,1,2-triphenylsilazane of very low molecular weight (n about 2–3).

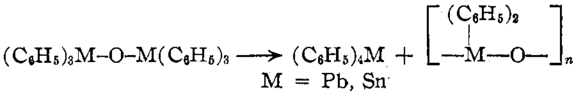


Pyrolyses of the triphenylgermanium azide and diphenylphosphinic azide both gave polymeric residues which contained phenyl groups bound to nitrogen (38.5% rearrangement for the germanium compound, 72% for the phosphorus compound). The vapor phase decomposition of benzenesulfonyl azide resulted in azobenzene in 17.5% yield and no other pure compounds or gums which contained phenyl groups bound to nitrogen.

The decomposition of the triphenyltin and lead azides yielded an entirely different result. Here a phenyl group migration proceeded from one metal atom to another in high efficiency.

$$(C_6H_5)_3MN_3 \longrightarrow N_2 + (C_6H_5)_4M \qquad M = Pb, Sn$$

Such a behavior is quite characteristic of phenyl–tin and –lead compounds. For example, the bis(triphenyltin) oxide[26] as well as the corresponding lead derivative[27] both undergo quantitative thermal rearrangements to yield the tetraphenyl compounds and polymeric diphenylmetal oxides.



$$(C_6H_5)_3M\text{-}O\text{-}M(C_6H_5)_3 \longrightarrow (C_6H_5)_4M + \left[\begin{array}{c}(C_6H_5)_2\\ |\\ -M-O-\end{array}\right]_n$$

M = Pb, Sn

TABLE I

APPROXIMATE DECOMPOSITION TEMPERATURES OF AZIDES

Compound	Approx. decn. temp., °C.
$(C_6H_5)_3CN_3$	190
$(C_6H_5)_3SiN_3$	380
$(C_6H_5)_2Si(N_3)_2$	320
$C_6H_5Si(N_3)_3$	>325
$(C_6H_5)_3GeN_3$	375
$(C_6H_5)_3SnN_3$	300
$(C_6H_5)_3PbN_3$	200
$(C_6H_5)_2P(O)N_3$	>140
$C_6H_5SO_2N_3$	135
$(CH_3)_3SiN_3$	>250
$CH_3Si(N_3)_3$	180

The phenyl group migration from silicon, germanium, phosphorus, and sulfur to nitrogen seems to be a novel analog of the Schmidt reaction and of similar "electron-deficient nitrogen" migration reactions. In the triphenylsilyl azide case, the phenyl group migration appeared to be very efficient. The yield of migration product dropped from silicon to phosphorus to sulfur (98+%, 72%, 17.5%, respectively). Also, the azene character of the decomposition increased from silicon to sulfur. The thermal decomposition of triphenylsilyl azide resulted in no azene reaction products while benzenesulfonyl azide[7] gave only azene products (both liquid phase). This behavior also correlated with the sharp decrease in thermal stability of these compounds ($(C_6H_5)_3SiN_3$, 350–380°; $(C_6H_5)_2P(O)N_3$, >140°; $C_6H_5SO_2N_3$, about 135° decomposition temperatures). The decrease in stability across the periodic table can be interpreted in terms of the availability of empty 3d-orbitals with which the innermost azide nitrogen can form a dπ–pπ double bond and thereby stabilize itself.

In the silicon case all five 3d-orbitals are unoccupied; the phosphinic azide uses one 3d-orbital for O–P double bonding, the sulfonyl azide two 3d-orbitals. Therefore, it would stand to reason that additional dπ–pπ interaction due to $-\overset{\curvearrowright}{\ddot{N}}-M-$ double bonding would decrease from Si^{+4} to OP^{+5} to O_2S^{+6}. This possibility is illustrated by the decrease in double bond character of the M–Cl bond in the series $SiCl_4$, $POCl_3$, SO_2Cl_2.[28]

The decrease in the stability of the triphenylmetal azides on going down the periodic table (group IV) can also be interpreted in terms of the decrease in dπ–pπ bonding as one goes from silicon to lead.[31] In triphenylmethyl azide no M–N double bonding would

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[25] W. H. Saunders, Jr., and J. C. Ware, *J. Am. Chem. Soc.*, **80**, 3328 (1958).

[26] O. Schmitz-DuMont and H. Meyer, *Z. anorg. allgem. Chem.*, **248** 289 (1941).

[27] W. T. Reichle, unpublished observations.

[28] Difference in calculated single[29] and experimentally determined[30] bond distance (Å.): Si–Cl_4, 0.15; OP–Cl_3, 0.10; O_2S–Cl_2, 0.04.

[29] L. E. Sutton, "Interatomic Distances and Configuration of Molecules and Ions," The Chemical Society, Special Publication No. 11, London, 1958.

[30] A. F. Wells, "Structural Inorganic Chemistry," 3rd Ed., Clarendon Press, Oxford, 1962, pp. 54–56. No electronegativity correction was made in the addition of normal covalent radii.

[31] R. West, R. H. Baney, and D. L. Powell, *J. Am. Chem. Soc.*, **82**, 6269 (1960).

seem possible, in the triphenyllead azide none may exist. The decomposition temperatures of both compounds were about the same ($(C_6H_5)_3CN_3$, 180–190°; $(C_6H_5)_3PbN_3$, 190–200°) despite the fact that both reactions proceeded by different mechanisms and to different products.

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Triphenylazido Compounds of Group IVA Elements[1]

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The five compounds $(C_6H_5)_3MN_3$, where M = C, Si, Ge, Sn, and Pb, have been prepared and characterized, and a comparative study of their properties has been carried out. The Si, Ge, and Sn compounds are isomorphous. The C and Si compounds react with triphenylphosphine to give 1:1 complexes, which differ markedly in their properties; the structures of these complexes are discussed. The Si and Ge compounds also form stable phosphineimines, $(C_6H_5)_3MN{=}P(C_6H_5)_3$.

The first organometallic azides, $(C_6H_5)_2BiN_3$, $(C_6H_5)_3Bi(N_3)_2$, and $C_6H_5Tl(N_3)_2$, were reported by Challenger and Richards in 1934.[2] The literature contains no other references to organometallic azides until late 1961, when this field of research suddenly became active. Methods developed recently have made it possible to prepare triphenylmetal azides of all group IVA elements. This paper is concerned with the syntheses and properties of these compounds, with special reference to the influence of the metal atom on the azide group. Azdiotriphenylmethane, $(C_6H_5)_3CN_3$ (I), has been known since 1909.[3] Azidotriphenylsilane, $(C_6H_5)_3SiN_3$ (II), was reported independently by us,[4] by Wiberg, *et al.*,[5] and by Sundermeyer.[6] Azidotriphenylgermane, $(C_6H_5)_3GeN_3$ (III), has not previously been reported, but Luijten and co-workers[7] have prepared azidotriphenylstannane, $(C_6H_5)_3SnN_3$ (IV), while Lieber, *et al.*, have synthesized azidotriphenylplumbane, $(C_6H_5)_3PbN_3$ (V).[8] While our work was in progress a parallel study of triphenylazido compounds of group IV elements, with emphasis on their thermal decomposition, was being carried out by Reichle.[9]

Synthetic Methods.—Two general methods for azide preparation were used. The first was originally used by Wiberg and Michaud[10] to prepare $Si(N_3)_4$, and later modified by Connolly and Urry[11] for the synthesis of $(CH_3)_3SiN_3$. The organometallic halide is refluxed with NaN_3 and $AlCl_3$ (forming $Al(N_3)_3$ *in situ*) in a dried organic solvent such as tetrahydrofuran, under a nitrogen atmosphere. Yields are usually greater than 50% and the method is quite general.

$$(C_6H_5)_3MX + NaN_3 \xrightarrow[\text{THF}]{AlCl_3} (C_6H_5)_3MN_3 + NaX\ (X = Cl, Br) \qquad (1)$$

Baldwin and Washburn[12] modified this method somewhat by eliminating $AlCl_3$ and using electron-rich organic solvents, such as acetonitrile, pyridine, or benzene. Lithium azide in pyridine has also been used.[5] We have found that this modified method works well for more reactive silyl halides [*e.g.*, $(CH_3)_3SiCl$, $(C_6H_5)_2SiCl_2$] in any of the proper solvents, and also for $(C_6H_5)_3MX$, provided pyridine is used as solvent. There is little reaction between $(C_6H_5)_3MX$ and NaN_3 in benzene.

The second general method was that employed by Luijten.[7] This reaction is more convenient than the first, but also more limited in scope. Sodium azide, dissolved in water, is shaken with an ethereal solution of the organometallic halide. Hydrolysis provides hydrazoic acid, the actual azidizing agent, which passes into the ether layer and reacts with the organometallic hydroxide.

$$(C_6H_5)_3MOH + HN_3 \xrightarrow{\text{ether}} (C_6H_5)_3MN_3 + HOH \qquad (2)$$

$$(C_6H_5)_3MX + 2H_2O \longrightarrow (C_6H_5)_3MOH + H_3O^+ + X^- \qquad (2a)$$

$$N_3^- + H_3O^+ \longrightarrow HN_3 + H_2O \qquad (2b)$$

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