

phenylethyl)trimethylsilane (7, 21%). Preparative vapor-phase chromatography (2% Apiezon L on Chromosorb W, 5 ft × 0.25 in., 230 °C) provided an analytically pure sample of silane 7: IR (liquid film) 1245, 860, 840, 698 cm⁻¹; ¹H NMR (80 MHz, CDCl₃) δ 0.00 (s, 9 H), 2.41 (t, 1 H, *J* = 7 Hz), 3.10 (d, 2 H, *J* = 7 Hz), 7.1 (m, 10 H); mass spectrum, 254 (14), 180 (68), 73 (100), 59 (20). Anal. Calcd for C₁₇H₂₂Si: C, 80.25; H, 8.72. Found: C, 80.38; H, 8.66.

Pyrolysis of the Lithium Salt 9 of 4-Methylbenzenesulfonic Acid 1-(Trimethylsilyl)hydrazide (4). At 0 °C under N₂ a stirred solution of (trimethylsilyl)hydrazide 4¹¹ (635 mg, 2.46 mmol) in tetrahydrofuran (5 mL) was treated dropwise with butyllithium (1.00 mL, 2.48 M in hexane, 2.48 mmol). Volatiles were then removed from the golden-yellow solution by evaporation at 25 °C in a stream of N₂, and the residue was dried under vacuum at 80 °C for 30 min. Pyrolysis of the dried residue at 170 °C (0.16 torr) produced lithium 4-methylbenzenesulfinate (10) as a white powder (377 mg, 2.33 mmol, 94.5%). This material was identical by IR with an authentic sample prepared by neutralization of 4-methylbenzenesulfonic acid with aqueous lithium hydroxide, and it could be converted quantitatively into 4-methylbenzenesulfonic acid by neutralization with aqueous sulfuric acid.

Pyrolysis of Lithium Hydrazide 9 in the Presence of Benzophenone. Lithium hexamethyldisilazide was prepared by treating a cold (0 °C) mixture of hexamethyldisilazane (150 μL) and tetrahydrofuran (1.5 mL) with butyllithium (340 μL, 2.13 M in hexane, 0.724 mmol) under N₂. This solution was then added dropwise during 5 min to a cold (0 °C), stirred solution of (trimethylsilyl)hydrazide 4¹¹ (180 mg, 0.696 mmol) in tetrahydrofuran (3 mL). A solution of benzophenone (40.4 mg, 0.222 mmol) in tetrahydrofuran (2 mL) was added, and the mixture was warmed at reflux for 44 h. During this period, lithium 4-methylbenzenesulfinate (10) precipitated and the color of the slurry faded from deep blue to white. Then the slurry was diluted with ether (15 mL) and centrifuged. Evaporation of the supernatant under reduced pressure left a residue of oil which could be resolved by preparative thin-layer chromatography (silica, benzene) into only one significant component, (diphenylmethoxy)trimethylsilane (15; 27.3 mg, 0.106 mmol, 48.0%, *R_f* 0.72). The IR, NMR, and mass spectra were identical with those of an authentic sample.²⁰

Pyrolyses of lithium hydrazide 9 in the presence of other compounds were conducted in a similar manner.

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Registry No. 4, 58971-25-8; 6, 72784-68-0; 7, 3528-07-2; 9, 72827-06-6; 10, 16844-27-2; 15, 14629-59-5; diphenylacetylene, 501-65-5; 1,2-diphenylethane, 612-00-0; benzophenone, 119-61-9.

Reaction of Triphenyl Phosphite with Elemental Bromine and Chlorine

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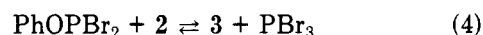
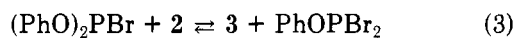
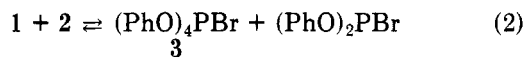
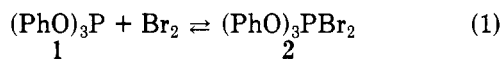
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The reaction between triphenyl phosphite and bromine was first investigated by Noack in 1883.¹ Since then the reaction of triaryl phosphites with halogens has been studied by numerous authors.^{2a-g} At ambient and higher

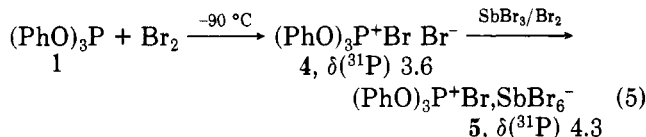
temperatures the reaction between triphenyl phosphite and bromine was recently explained by Tseng^{2g} by the series of equilibria shown in eq 1-4. In connection with



our study on the Arbuzov reaction between phosphites and halogens,³ the reaction between triphenyl phosphite and halogens was reinvestigated with the aid of low-temperature FT ³¹P NMR spectroscopy.

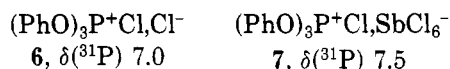
Results and Discussion

Triphenyl phosphite (1) reacts with elemental chlorine and bromine at temperatures well below room temperature. In liquid nitrogen no detectable reaction takes place, making it possible to keep substrates together unreacted. In a typical experiment, triphenyl phosphite (1) was dissolved in nitropropane or methylene chloride. After the solution was cooled in liquid nitrogen, an equimolar quantity of the halogen was added. When the temperature had risen to -90 °C, the ³¹P NMR spectrum clearly indicated the formation of only one product with a chemical shift value typical of the phosphonium salts containing three oxygen ligands [δ(³¹P)] 3.6 for 4 and δ(³¹P)] 7.0 for 6]. It clearly established that the charge on the phosphorus molecule with phosphorus in a given valence state has little effect on the magnetic shielding at the phosphorus atom.^{3b,c,4} The phosphonium structure of the product 4 is strongly supported by the fact that it has been possible to transform the salt 4 (eq 5) into a relatively stable



phosphonium hexabromoantimonate which displays in the ³¹P NMR spectrum an almost identical chemical shift value with that of 5. This reaction is carried out by treating the reaction mixture with equimolar amounts of SbBr₃ and Br₂.

Identical results are obtained in the case of the product obtained during the low-temperature chlorination of 1. The ³¹P NMR δ value of the product formed and the reaction with SbCl₅ also indicate the phosphonium structure 6. This is in full agreement with our previous studies in



which it was possible to demonstrate that under conditions

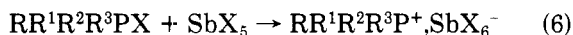
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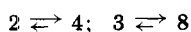
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similar to those used in this investigation there is little interaction within the ion pair involved in the phosphonium salt.^{3b} In the case of a phosphorane structure 2, one should expect a dramatic change in chemical shift after addition of antimony pentachloride due to a transformation into a lower coordination state as clearly demonstrated before with the aid of suitable models⁵ (eq 6).



The phosphonium hexachloroantimonate 7 was isolated at -10°C as colorless crystals which were sensitive to air or moisture. The phosphonium hexabromoantimonate 5 and its chlorine analogue 7 are stable at ambient temperature, owing to the low P nucleophilicity of the counterion, and do not undergo subsequent changes leading to a complex mixture as is observed for 4 and 6. The compounds of the phosphonium structure 4 and 6 are also present in the reaction of 1 with halogens at room temperature. For example, in our hands the reaction between 1 and equimolar amounts of elemental bromine under this condition gave the same ^{31}P NMR spectrum as given by Tseng. After 0.5 h at 20°C two major peaks, $\delta(^{31}\text{P})$ 2.8 and $\delta(^{31}\text{P})$ -22.6 , were observed which must be ascribed to the phosphonium salt 4 and another phosphonium salt $(\text{PhO})_4\text{P}^+\text{Br}^-$ (8).⁶

For this reason the scheme of Tseng^{2g} presented in the introduction of this paper should be amended by adding to the equilibrium equation containing the phosphorane structures 2 and 3, an equilibrium reaction further illustrating the collapse of 2 and 3 into their respective phosphonium species 4 and 8. This equilibrium should be strongly shifted in favor of the phosphonium structure:



Experimental Section

General Methods. All solvents were purified by conventional methods. All reactions were carried out in sealed tubes, and standard vacuum techniques were used throughout. ^{31}P NMR spectra were recorded at 24.3 MHz with a JEOL R-60H spectrometer operating in the pulsed FT mode. A heteronuclear spin decoupler, JNM-SD-HC, was used for chemical shift determinations and integration. All spectra were recorded on samples which were approximately 0.5 M in reagent, i.e., 0.001 mol of the compound in 2 mL of a solvent. The chemical shifts downfield from the 85% phosphoric acid standard are reported as positive values and those upfield as negative values.

Chlorotriphenoxyphosphonium Hexachloroantimonate (7). To a stirred solution of triphenyl phosphite (3.1 g, 0.01 mol) in methylene chloride-ether (3:1, 6 mL) at -78°C under argon is added elemental chlorine (0.71 g, 0.01 mol). The mixture is stirred for 10 min, and then antimony pentachloride (3 g, 0.01 mol) in methylene chloride (2 mL) is added over 20 min at -78°C . The white crystals which separated at -10°C are washed with anhydrous ether to yield 7 (5.05 g, 75%). Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{Cl}_7\text{O}_3\text{PSb}$: C, 31.8; H, 2.25; P, 4.55; Cl, 36.5. Found: C, 31.65; H, 3.0; P, 3.50; Cl, 36.5.

Registry No. 1, 101-02-0; 7, 18556-97-3; chlorine, 22537-15-1; bromine, 10097-32-2.

(5) For example: R, R¹ = *o*-phenylene and R² = R³ = X = Br [$\delta(^{31}\text{P})$ -189 (P^V), $\delta(^{31}\text{P})$ 20.6 (P^{IV})], J. Gloede and H. Gross, *J. Prakt. Chem.*, **320**, 140 (1978); R, R¹ = *o*-phenylene, R² = OEt, and R³ = X = Br [$\delta(^{31}\text{P})$ -104 (P^V), $\delta(^{31}\text{P})$ 37 (P^{IV})].^{3c}

(6) The chemical shift value for 8 is identical with that of the phosphonium cation described by other authors: L. Kolditz, K. Lehmann, W. Wicker, and A.-R. Grimmer, *Z. Anorg. Allg. Chem.*, **360**, 259 (1968); L. V. Nestorov, R. I. Metalopova, S. G. Salikhov, and E. I. Loginova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 414 (1971); H. Teichmann and M. Jatkowski, *J. Prakt. Chem.*, **314**, 125 (1972).

Conformational Analysis Utilizing Carbon-13-Carbon-13 Spin-Spin Coupling Constants: Diamantane (Congressane) Derivatives

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Ever since the suggestion was made that ^{13}C - ^{13}C coupling constants might parallel geometrically equivalent proton-proton coupling constants,^{1,2} a natural goal was to establish such a correlation between vicinal carbon-carbon and proton-proton couplings³ and to proceed to conformational analysis by utilizing carbon-carbon J values.⁴ Employing carbon-carbon coupling constants, instead of proton-proton coupling constants,⁵ would have the advantage in conformational analysis of utilizing a phenomenon that involves the four-carbon chain in question throughout its length. Accordingly, it might be anticipated that carbon-carbon couplings would give more accurate information regarding the conformation of the carbon chain. Also, a successful correlation of J_{CC} and the dihedral angle⁶ could be used in the conformational analysis of systems that would not be amenable to proton NMR analysis (whether because of no hydrogens, too many hydrogens, or hydrogens substituted in the wrong places). However, because of additional bonding electrons, carbon-13 couplings might be susceptible to a greater number of complications; and, indeed, some difficulties were noted⁷ in an attempt to establish a J_{CC} /dihedral angle correlation, particularly in adamantane derivatives.^{8,9} It therefore became of interest to see if these "anomalous" results were unique or were characteristic of certain cage-like molecules. Accordingly, in the present study we synthesized analogous diamantane (*two* fused adamantanes) derivatives 2 and 3 (see Table I) and determined the corresponding carbon-carbon coupling constants.

Results and Discussion

Synthesis of 1-diamantanecarboxylic acid- ^{15}C (2) was accomplished by recycling carbon- ^{13}C monoxide through 1-bromodiamantane dissolved in sulfuric acid. Compound 2 was then carried on to 1-(hydroxymethyl)diamantane- ^{15}C (3) by lithium aluminum hydride reduction.

Carbon-13 chemical shift assignments for 2 were made by integration (one carbon vs. two carbons), comparison of δ values with the parent compound diamantane (1), by use of CW off-resonance decoupling, and observation of carbon-carbon splitting; and, fortunately, through this combination of methods all assignments could be made unambiguously and securely. For the utilization of the δ values of 1, misassignments in the literature¹⁰ had to be

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