

the volatile perfluorocyclooctatetraene were obtained. The first weighed 8.15 g (mp 40–42.5 °C, ~97% pure by GLC) and the second weighed 0.60 g (mp 40–41.5 °C, ~94% pure by GLC). These crystals represent a 42% yield (uncorrected for impurities) based on photoadducts and thus a 25% overall yield from perfluorobenzene.

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Registry No. 1, 57070-35-6; 2, 72726-96-6; 3, 72726-97-7; 4, 72777-10-7; 1,2-dichloro-1,2-difluoroethylene, 598-88-9; perfluorobenzene, 392-56-3.

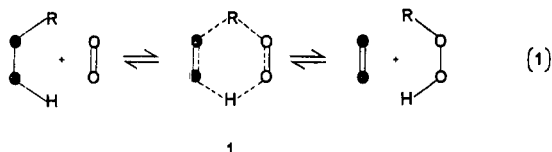
Transfer of Hydrogen from (Trimethylsilyl)diazene

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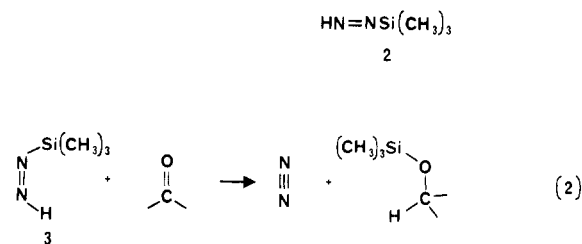
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Structure 1 is a generalization of plausible transition states for the transfer of hydrogen during Meerwein-Ponndorf-Verley reductions,¹ Cannizzaro reactions,² reductions by Grignard reagents,³ hydrogenations by *cis*-9,10-dihydronaphthalene⁴ and diazene,⁵ and other related reactions.⁶ If ●=● is a volatile molecule with a low heat



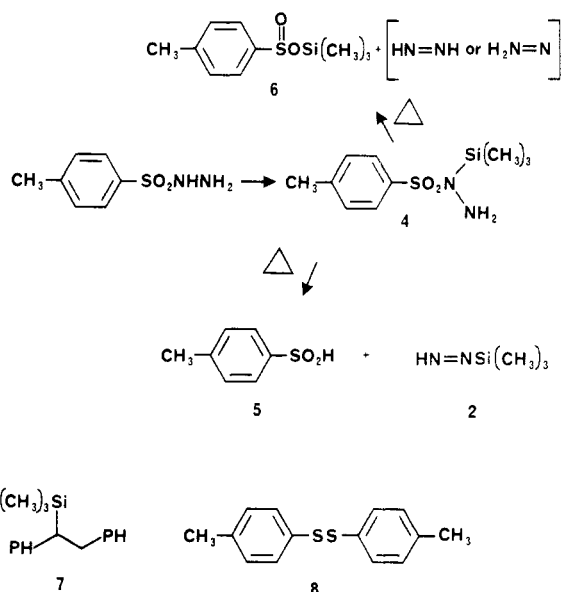
of formation which contributes to the stabilization of transition state 1, then reaction 1 should be rapid and virtually irreversible. In reductions of symmetrical multiple bonds by diazene, for example, transfer of hydrogen and formation of nitrogen are coupled effectively.^{5,7} Reductions of the polar double bonds of aldehydes and ketones by diazene commonly are much less efficient, however,⁸ but we hoped that the great strength of single bonds between silicon and oxygen⁹ would make (trimethyl-

silyl)diazene (2) a more effective agent for the reduction of carbonyl compounds (eq 2). Note that synchronous



transfer of the elements of trimethylsilane requires (*Z*)-(trimethylsilyl)diazene (3). Evidence for the geometrical isomerization of diazene itself in the gas phase¹⁰ suggested that both (*Z*)- and (*E*)-(trimethylsilyl)diazene might serve as agents for the transfer of hydrogen and encouraged us to try the experiments described below.

We hoped that pyrolysis of 4-methylbenzenesulfonic acid 1-(trimethylsilyl)hydrazide (4) would generate (trimethylsilyl)diazene and 4-methylbenzenesulfinic acid (5).



The reaction of 4-methylbenzenesulfonic acid hydrazide with equimolar amounts of triethylamine and chlorotrimethylsilane (THF, 25 °C) efficiently produced hydrazide 4,¹¹ but pyrolysis of this compound at 170 °C (0.10 torr) yielded primarily trimethylsilyl 4-methylbenzenesulfinate (6, 64%).¹² Its infrared spectrum included a strong band at 1140 cm⁻¹ characteristic of the esters of sulfinic acids,¹³ and hydrolysis in aqueous THF at 25 °C quantitatively converted sulfinate 6 into sulfinic acid 5. Since pyrolysis of (trimethylsilyl)hydrazide 4 at 170 °C in diglyme in the presence of diphenylacetylene provided 1,2-diphenylethane (57%), diazene⁵ or isodiazene¹⁴ presumably are among the primary products of decomposition. Formation of (1,2-diphenylethyl)trimethylsilane (7, 21%)¹² under these conditions suggested that a competing mode of decom-

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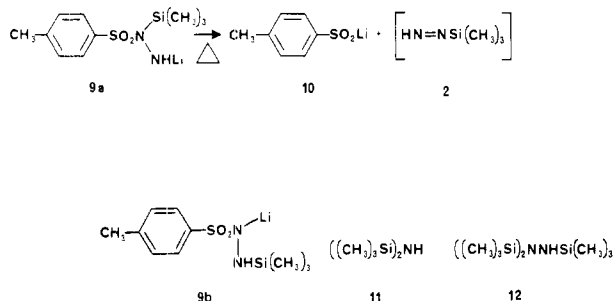
(12) The assigned structure was consistent with the elemental analysis and the IR, NMR, and mass spectra of this new substance.

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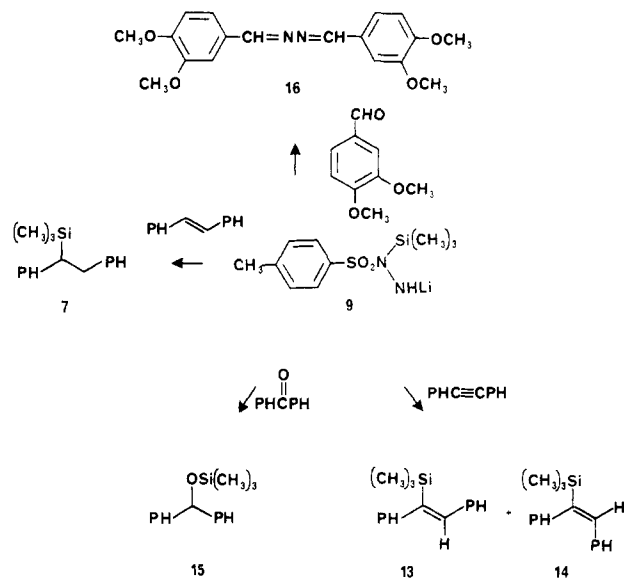
position had produced sulfinic acid 5 and (trimethylsilyl)diazene (2), which then transferred the elements of trimethylsilane to diphenylacetylene or stilbene. Evidence for the intermediacy of sulfinic acid 5 was provided by the isolation of one of the products of its decomposition, bis(4-methylphenyl) disulfide (8).¹⁵

For a superior source of (trimethylsilyl)diazene, we turned to the lithium salt of (trimethylsilyl)hydrazide 4, prepared by treating the hydrazide with butyllithium or lithium hexamethyldisilazide in THF at 25 °C and tentatively assigned structure 9a or 9b.¹⁶ Pyrolysis of this



salt at 140 °C (0.18 torr) produced lithium 4-methylbenzenesulfinate (10, 95%) and liberated a gas, possibly containing (trimethylsilyl)diazene, which was condensed at -78 °C. Initially a blue liquid, this condensate rapidly and irreversibly faded at 0 °C and evolved a small volume of gas. Hexamethyldisilazane (11, 31%) and tris(trimethylsilyl)hydrazine (12, 5%)¹⁷ were the major isolable components of the final product, and no trimethylsilane could be detected. Free-radical reactions convert bis(trimethylsilyl)diazene into compounds 11 and 12 above -30 °C and may also be responsible for the decomposition of (trimethylsilyl)diazene.¹⁸

When a solution of lithium hydrazide 9 in THF was heated at 65 °C, lithium sulfinate 10 slowly and quantitatively precipitated. Addition of (*E*)-1,2-diphenylethene did not change the rate of decomposition, but the alkene was converted cleanly into (1,2-diphenylethyl)trimethylsilane (7, 32%),¹² possibly by the action of trimethylsilyldiazene. A similar decomposition of lithium hydrazide 9 in the presence of diphenylacetylene yielded a mixture of (*Z*)-(1,2-diphenylethenyl)trimethylsilane (13, 10%)¹⁹ and (*E*)-(1,2-diphenylethenyl)trimethylsilane (14, 27%).¹⁹ Since these substances were not interconverted during the reaction, transfer of the elements of trimethylsilane from (trimethylsilyl)diazene to alkenes and alkynes cannot be synchronous. Pyrolysis of excess lithium hydrazide 9 in THF in the presence of benzophenone, which did not affect the rate of decomposition, produced lithium sulfinate 10 (95%) and (diphenylmethoxy)trimethylsilane (15, 48%).²⁰ By similar procedures, aldehydes and aliphatic ketones were not reduced efficiently but were converted instead into the corresponding azines. For example, decomposition



of lithium hydrazide 9 in the presence of 3,4-dimethoxybenzaldehyde produced azine 16 (43%).²¹

If (trimethylsilyl)diazene (2) is responsible for these reactions, it does in fact transfer the elements of trimethylsilane to some alkenes, alkynes, and aryl ketones, but not in general by the synchronous process of reaction 1; instead, diazene 2 appears to serve as a source of the trimethylsilyl radical.

Experimental Section

All infrared (IR) spectra were recorded on a Perkin-Elmer Model 137 spectrometer. Varian T-60 and HFT-80 spectrometers were used to obtain ¹H nuclear magnetic resonance (NMR) spectra. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane (δ). All mass spectra were recorded at 70 eV on an AEI MS-9 double-focusing spectrometer; the ratio *m/e* and the relative intensity are reported in the form *m/e* (relative intensity). A Varian Aerograph Model 1420 instrument was used for preparative and analytical vapor-phase chromatography. Galbraith Laboratories, Knoxville, TN, performed all elemental analyses. Glassware was dried at 120 °C and cooled under dry N₂ immediately before use. Tetrahydrofuran was distilled from the sodium ketyl of benzophenone, diglyme was distilled from LiAlH₄, and hexamethyldisilazane was distilled under dry N₂ at atmospheric pressure before use. All other reagents were commercial products of the highest purity obtainable.

Pyrolyses of 4-Methylbenzenesulfonic Acid 1-(Trimethylsilyl)hydrazide (4). (a) A neat sample of (trimethylsilyl)hydrazide 4¹¹ (3.35 g, 13.0 mmol) was heated at 170 °C under vacuum (0.10 torr) in a short-path still. The major product of decomposition, trimethylsilyl 4-methylbenzenesulfinate (6), was a colorless liquid boiling at 130 °C (0.10 torr) (1.90 g, 8.32 mmol, 64.0%). Redistillation at 73–77 °C (0.006 torr) provided a purified sample: IR (liquid film) 1255, 1140, 850, 762 cm⁻¹; ¹H NMR (60 MHz, CDCl₃) δ 0.41 (s, 9 H), 2.47 (s, 3 H), 7.47 (d of d, 4 H); mass spectrum, 228 (56), 180 (79), 165 (23), 150 (31), 149 (100), 73 (95); high-resolution mass spectrum *m/e* 228.3783 (calcd for C₁₀H₁₆O₂Si 228.3770).

(b) A solution of (trimethylsilyl)hydrazide 4¹¹ (1.58 g, 6.13 mmol) and diphenylacetylene (0.138 g, 0.777 mmol) in diglyme (5 mL) was heated at 170 °C under N₂ for 1 h. Then the solution was cooled and added to basic aqueous H₂O₂ (16 mL of 1.0 N NaOH, 2 mL of 30% H₂O₂). This mixture was extracted with ether, and evaporation of the dried extracts left a residue of yellow oil. Preparative thin-layer chromatography (silica, CCl₄) resolved a single major band (*R_f* 0.6) which consisted (analysis by NMR and by vapor-phase chromatography on Apiezon L) of 1,2-diphenylethane (57% from diphenylacetylene) and (1,2-di-

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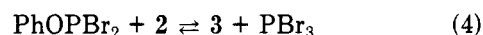
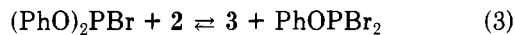
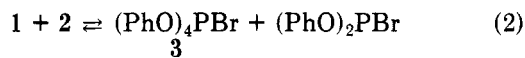
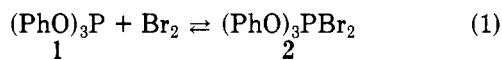
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The reaction between triphenyl phosphite and bromine was first investigated by Noack in 1883.¹ Since then the reaction of triaryl phosphites with halogens has been studied by numerous authors.^{2a-g} At ambient and higher

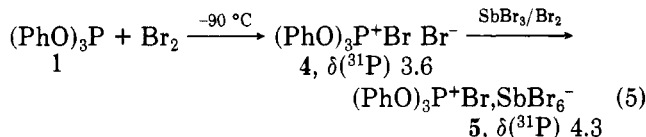
temperatures the reaction between triphenyl phosphite and bromine was recently explained by Tseng^{2g} by the series of equilibria shown in eq 1-4. In connection with



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.

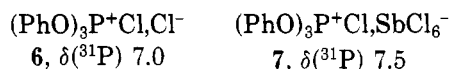
Results and Discussion

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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