Deoxygenation of Aryl Nitro Compounds with Disilanes

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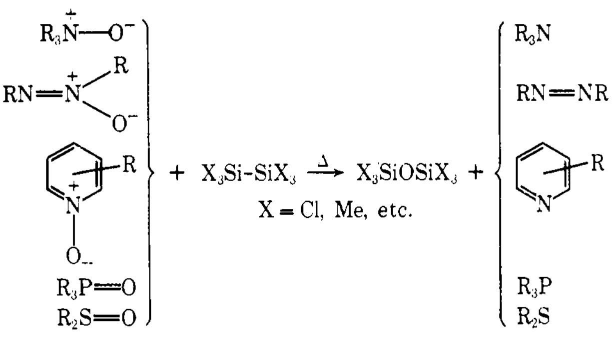
Disilanes have been found to represent a new class of deoxygenating agents for aryl nitro compounds. Semiquantitative investigation of the effect of disilane structure on the deoxygenation of 2-nitrobiphenyl (**1**) at 240°, which yielded 2-aminobiphenyl (**3**) and carbazole (**4**), indicated only moderate reduction rate differences among those disilanes studied, with hexachlorodisilane (Si_2Cl_6) and hexaphenyldisilane (Si_2Ph_6) being the most and least reactive, respectively. In contrast, the relative ratio of **4**:**3** was markedly dependent on disilane structure and varied between limits of ~70:1 and 1:35 for reduction with, respectively, cyclic 1,2-disilacyclopentene derivative **6** and Si_2Cl_6. Deoxygenation of nitrobenzene (**7a**), *o*-nitrotoluene (**7b**), and *p*-nitrotoluene (**7c**) with hexamethyldisilane (Si_2Me_6) gave their corresponding amines and azo coupling products, with $\Delta G^{\ddagger}_{220°} = 41$ kcal/mol for the pseudo-first-order reduction of **7a** in excess Si_2Me_6. Qualitative comparison of Si_2Me_6 deoxygenation rates for **1** and **7a–c** at 240° revealed that relative substrate reactivities were not in accord with expectations based on simple steric considerations. Failure of 2-nitrosobiphenyl to undergo deoxygenation by Si_2Me_6 has led to the suggestion that disilane reduction of **1** and, by extension, other nitro aromatics does not proceed in a stepwise fashion *via* nitroso intermediates. Mechanisms which accommodate this restriction and account for the observed stoichiometry and products are discussed in terms of possible transient nitrene species. Attempts to carry out low-temperature photochemical deoxygenation of **1** with Si_2Me_6 proved unsuccessful.

Deoxygenation of nitro compounds (RNO_2) with appropriate reducing agents can, in principle, lead to generation of nitrenes ($R\ddot{N}:$) as transitory reaction intermediates (eq 1). Early attempts to utilize metallic salts[2] for this reduction process have been followed by more recent work with metal carbonyls;[3] however, the majority of synthetic[4] and mechanistic[5] investigations related to eq 1 have employed Cadogan's[4a] phosphine method (eq 2) to effect nitro group deoxygenation. The proven ability of disilanes ($X_3Si{-}SiX_3$) to function as efficient reducing agents for various organic[6a,c,7] (and inorganic[8]) nitrogen oxides, as well as phosphine oxides[6a,6b] and sulfoxides[6a] (eq 3), suggested to us that disilanes might also serve as useful deoxygenating agents for nitro compounds.[9] In addition to the possibility that such a process might hopefully proceed at temperatures lower than those necessary with known nitro group reducing reagents, other advantages were envisaged. Thus, use of disilanes would preclude complications due to extensive formation of unwanted phosphorimidate ($RN{=}PR_3'$) side products,[4b,10] which oftentimes accompany reduction with phosphorus reagents, and limitations placed on deoxygenation of multifunctional nitro compounds due to the well-known[11] reactivity of phosphines toward halide, epoxide, and keto groups might also be removed by use of nonnucleophilic disilane reagents. With these potential benefits in mind, we undertook the exploratory investigation of nitro group reduction by disilanes that is presented in the following sections.[12]

$$RNO_2 \longrightarrow R\ddot{N}: \longrightarrow \text{products} \qquad (1)$$

$$RNO_2 + 2R_3'P \longrightarrow R\ddot{N}: + 2R_3'PO \qquad (2)$$



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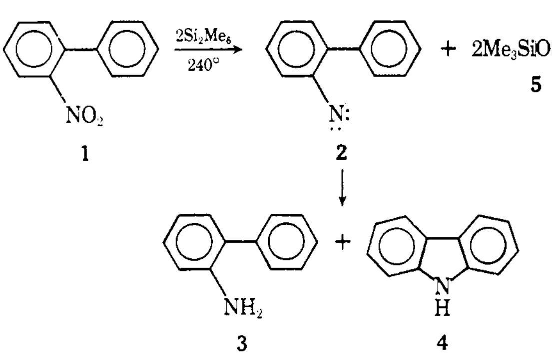
Results and Discussion

Deoxygenation of 2-Nitrobiphenyl with Hexamethyldisilane. Commercially available hexachlorodisilane (Si_2Cl_6) has been generally used in disilane deoxygenation studies;[6] however, the somewhat detrimental characteristics (H_2O and O_2 sensitivity) of this reagent relative to hexamethyldisilane (Si_2Me_6), which is readily prepared[13] and convenient to handle, led to selection of Si_2Me_6 for initial evaluation. Our choice, like others,[3a,4a,14] of 2-nitrobiphenyl (**1**) as a prototypal substrate for deoxygenation was prompted by the expectation that the nitrene (or nitrenoid) intermediate derived therefrom, *viz.* 2-biphenylylnitrene (**2**), would produce thermally stable products from relatively well-defined reaction modes: 2-aminobiphenyl (**3**) from H abstraction and carbazole (**4**) *via* formal intramolecular C–H bond insertion (*cf.* eq 4). Nitroalkanes were not considered in the present study since similar reaction modes with alkylnitrenes possessing α-hydrogens are generally low-yield events, due to efficient competition by intramolecular α-hydrogen abstraction[15] yielding imines which subsequently undergo rapid polymerization.



(4)

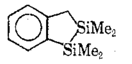
As indicated by eq 4, deoxygenation is simply achieved by heating an *o*-dichlorobenzene (ODCB) solution of **1** (0.7 *M*) containing 2 molar equiv of Si_2Me_6 (1.4 *M*) at 240° for *ca.* 2 hr, using a sealed (*in vacuo*) glass ampoule. Analysis (vpc) of the darkened reaction mixture revealed that only a small percentage (~10%) of unchanged starting material remains under these conditions and that near-quantitative production of hexamethyldisiloxane (**5**) occurred. Work-up led to isolation of **4** (42%) as the major product and a small amount of **3** (4%). Only a trace amount (<1%) of an addi-

Table I
Deoxygenation of 2-Nitrobiphenyl (1) with Various Reagents

Reagent	Reagent:1, molar ratio	Conditions	Product, %[a] 4	3
Si_2Me_6[b]	2	240°, 2.5 hr	42	4
$(EtO)_2PMe$[c]	4	100°, 2 hr	85	Not reported
FeC_2O_4[d]	13	210°, 0.5 hr	63	Not reported
$Fe(CO)_5$[e]	1.4	142°, 24 hr	15	58

[a] Isolated yield. [b] This work. [c] Reference 5c. [d] Ferrous oxalate, ref 14. [e] Reference 3a.

Table II
Deoxygenation of 2-Nitrobiphenyl (1) with Disilanes[a]

Disilane	Registry no.	Unreacted 1, %[b]	Product, %[b] 4	3
Si_2Ph_6	1450-23-3	100[c]		
Si_2Me_6	1450-14-2	90	4	1
$Si_2Me_5(OPh)$	32286-27-4	85	6	1
$Si_2Me_5(Ph)$	1130-17-2	27	37	7
	40662-22-4	22	71	1
Si_2Cl_6[d]	13465-77-5	13	10	47

[a] Sealed ampoule with o-dichlorobenzene (ODCB) solvent; [1] = 0.7 M; [disilane] = 1.4 M; 240°, 1.5 hr. [b] Determined by quantitative vpc after addition of triphenylmethane internal standard and corrected for thermal conductivity differences. [c] 95% after 15 hr, with 5% 4 and no detectable (<1%) 3. [d] Vpc analysis preceded by alkaline work-up of reaction mixture.

tional and as yet unknown compound was detectable by vpc.

More accurate appraisal of the true product distribution by vpc techniques gave 86% conversion of 1 into 68% 4 and 8% 3, with ~20% material loss attributable to intractable "tars," which were evident by tlc and are commonly encountered[4] in nitrene chemistry. Appropriate control experiments confirmed that neither starting material 1 nor a 1:1:2 mixture of 3:4:Si_2Me_6 (or 3:4:5) react significantly under the reduction conditions employed. These facts suggest that the deoxygenation stoichiometry is as shown in eq 4, which is a conclusion consistent with earlier studies[6a,7] indicating that each Si–Si linkage in a polysilane is capable of extruding one oxygen atom from the oxidant.

Comparison of the above data with typical results reported for other deoxygenating agents (Table I) indicated that Si_2Me_6 competes reasonably well with ferrous oxalate and is superior to $Fe(CO)_5$ for production of the synthetically more significant ring closure product 4, but is not as efficient as the phosphonite reagent.

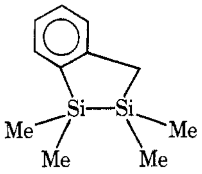
Attempts to investigate possible acceleration of the disilane deoxygenation rate of 1 by solvent variation were restricted by the unavailability of media which are considered to be strongly solvating but yet inert toward Si_2Me_6 at elevated temperatures. This dual criterion excludes solvents such as hexamethylphosphoramide (HMPA) and dimethyl sulfoxide (DMSO), as well as various alcohols. Consequently, it was not surprising that substitution of ODCB with either n-nonane, p-xylene, chlorobenzene, or bromobenzene, which are all relatively nonpolar substances, resulted in little or no improvement on reduction velocity.[16]

Modification of Disilane Structure. Variously substituted acyclic disilanes (Table II) and the novel 1,2-disilacyclopentene derivative 6[17] were next explored in order to (a) assess those structural features which might afford increased deoxygenating capacity toward 1 and (b) possibly elucidate mechanistic aspects of the reduction under consideration. Moreover, there has been only one systematic investigation[7] of disilane structure with regard to deoxygenation potency, and this was primarily restricted to remote electronic effects of ring substituents in phenoxypentamethyldisilane [$Si_2Me_5(OPh)$] derivatives.

Table III
Deoxygenation of Aryl Nitro Compounds with Si_2Me_6[a]

Compd	Rxn time, hr	Unreacted compd, %[b]	Products Amine (%)	Azo (%)
1	13	0	4 (67[c])	Not determined
7a	43	16[c]	8a (22[c])	9a (11[c])
7b	42	22	8b (14)	Not determined
7c	45	50	8c (30)	9c (10)

[a] Sealed ampoule; molar ratio compound:Si_2Me_6 = 1:3, no solvent; 240°. [b] Determined by quantitative vpc with addition of authentic material, unless specified otherwise. [c] Isolated yield.



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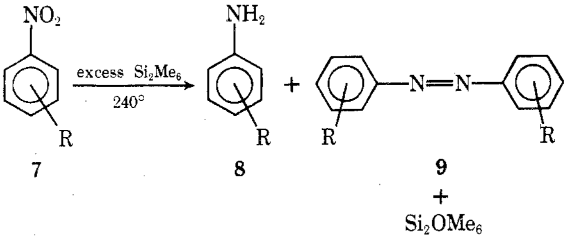
The relative amounts of unreacted 1 listed in Table II indicate that only moderate deoxygenation rate differences obtain for the disilanes studied, with the exception of hexaphenyldisilane (Si_2Ph_6), which was effectively inert under the specified standard reaction conditions.[18] These *roughly* comparable deoxygenation rates for 1 stand in contrast to dramatic disilane reduction rate inequities which may be extracted from available literature data. Thus, we estimate that $Si_2Me_5(OPh)$ is on the order of 1000 times more reactive than Si_2Me_6 toward conversion of trimethylamine oxide to trimethylamine[7] and that Si_2Cl_6 is capable of reducing phosphine oxides ~500 times faster than Si_2Me_6.[6a] It may therefore be concluded that those factors which render $Si_2Me_5(OPh)$ and Si_2Cl_6 considerably more reactive than Si_2Me_6 in amine and phosphine oxide deoxygenations, respectively, are unimportant in the present context. In similar fashion, the enhanced reactivity (>95-fold) of "strained"[17,19] disilane 6 over acyclic model compound $Si_2Me_5(Ph)$ toward Si–Si bond oxidation by m-chloroperbenzoic acid is not translated into a comparable deoxygenation rate difference toward 1 (*cf.* Table II).

Deoxygenation of Other Nitro Compounds with Hexamethyldisilane. Reactions at the ortho position in biphenyl systems may, on account of steric effects, be subject to pronounced rate retardation. It was of interest, therefore, to determine whether sterically less encumbered nitro groups, relative to that in 1, undergo disilane deoxygenation under more mild reaction conditions.

Reduction of 7a–c with Si_2Me_6 (eq 5) gave the expected



(5)

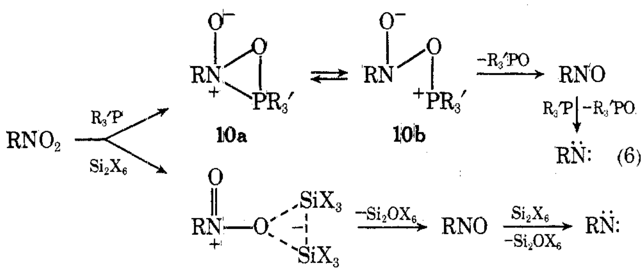
a, R = H; b, R = o-Me; c, R = p-Me

amines as major products in addition to somewhat lower yields of azo coupling products (**9**) (Table III). However, in contrast to expectations based on simple steric arguments, comparison of reaction times and amounts of unreacted starting material listed in Table III for **1** *vs.* **7a** and **7c** reveals that deoxygenation of the more accessible nitro groups offered by **7a** and **7c** is actually slower than that for **1**. Unimportance of steric effects is similarly indicated by comparison of the data tabulated for **7b** and **7c**, since the crowded *o*-NO_2 group in the former system undergoes more extensive reduction than its para-positioned counterpart in **7c**. At this point, we can only speculate that "electronic factors" may play a dominant role in governing relative disilane deoxygenation rates.

Causative factors underlying the production of **9** are discussed in a following section dealing with mechanism.

Kinetic and Mechanistic Considerations. The kinetics for deoxygenation of aryl nitro compounds with disilanes were briefly studied using **7a** and Si_2Me_6 (20-fold molar excess) as model reactants. The pseudo-first-order rate constant (k') calculated for disappearance of **7a** from duplicate runs is $k'_{220°} = 5.6 \pm 0.1 \times 10^{-6}$ sec^{-1} ($\tau_{1/2} \simeq 34$ hr), which corresponds to $\Delta G^{\ddagger}_{220°} = 41$ kcal/mol. This value for $\Delta G^{\ddagger}$ is significantly lower than the ~51 kcal/mol energy of activation reported for thermal decomposition of **7a**[20] and other[21] aromatic nitro compounds into aryl and NO_2 radicals *via* initial C–N bond homolysis.[21,22] These facts, in conjunction with the demonstrable thermal stability of Si_2Me_6 under the present reaction conditions, lead us to conclude that free-radical disilane deoxygenation paths initiated by C–N and/or Si–Si bond fission are not likely.

Mechanistic studies of nitro group deoxygenation with phosphorus reagents have prompted the suggestion[5a-c] of a stepwise process (eq 6) involving monodeoxygenation of RNO_2 *via* **10** to produce nitroso intermediates (RNO), which then undergo relatively rapid deoxygenation to generate nitrenes (or nitrenoids). An analogous series of transformations (eq 7) is reasonable for disilanes, wherein **11** is similar to the intermediate (**12**) postulated[23] for disilane oxidation by peracids (eq 8).



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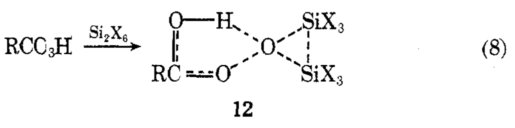

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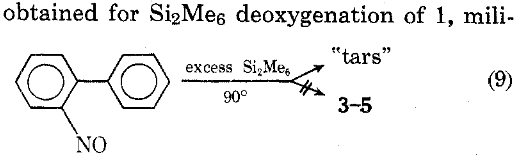
We have investigated the above possibility and have found that 2-nitrosobiphenyl (**13**) suffers essentially complete decomposition to mainly "tars," *without* forming detectable amounts of **3** or **4**, when heated at only 90° (19 hr) in ODCB containing a 20-fold molar excess of Si_2Me_6 (eq 9). These observations, coupled with high (80–90%) material balances obtained for Si_2Me_6 deoxygenation of **1**, militate against the intermediacy of **13** during reduction of **1** with disilanes and, hence, eq 7 or any other monodeoxygenation variant thereof.[24]



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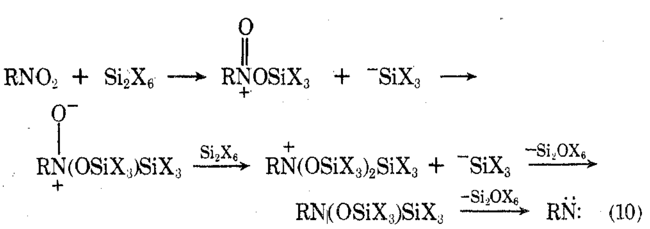
An alternative deoxygenation scheme, which bypasses nitroso compound intermediacy and is a simple extension of the disilane reduction mechanisms previously considered[6a,7] for amine oxides, is shown in eq 10. In this scheme



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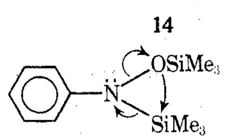
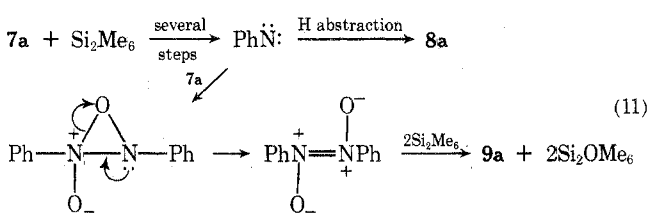


14a

initial nucleophilic attack[7] of RNO_2 at silicon and concomitant Si–Si bond heterolysis is pictured as being followed by a sequence of steps which features ultimate nitrene generation *via* α-elimination of disiloxane (Si_2OX_6) from bis(silyl)hydroxylamine intermediate **14**. We have recently obtained evidence that supports the feasibility of this novel "α-deoxysilylation" proess[25,26] (**14** → RN̈: + Si_2OX_6) and demonstrates, *inter alia*, that expulsion of Si_2OMe_6 from **14a** takes place rapidly ($\tau_{1/2} \simeq 4$ hr) at only ~100°, which is far below those temperatures needed for nitro group reduction by disilanes. Thus, to the extent that eq 10 actually reflects the mechanism for RNO_2 deoxygenation by disilanes, we conclude that the rate-limiting step occurs prior to fragmentation of **14**.

In an attempt to obtain more direct evidence for the involvement of **14** in the present reduction studies, **14a** was pyrolyzed in a threefold molar excess of Si_2Me_6 at 240°, which are the same conditions listed in Table III for Si_2Me_6 deoxygenation of **7a**. As expected on the basis of eq 5 and 10, **14a** yielded **8a** and **9a**; however, in contrast to the *ca.* 2:1 ratio of **8a**:**9a** obtained from **7a**, compound **14a** produced a *ca.* 4:1 mixture of these common products. As shown in eq 11, the relatively high yield of **9a** which is observed with **7a** may be rationalized by assuming that formation of **9a** involves addition of phenylnitrene to unreacted **7a**[29] followed by deoxygenation of **15**;[30] a similar path in the aforementioned study with **14a** is not operative. Consistent with this mechanistic rationalization, it was found that heating an equimolar mixture of **14a** and **7a** with Si_2Me_6 results in a substantial increase in the relative amount of **9a**, *viz.* **8a**:**9a** ≃ 1:1.



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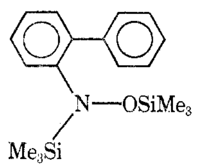
Comparative studies of **1** and Si_2Me_6 *vs.* **16**, which were considered as an additional probe for the validity of eq 10, have been foiled by our inability to prepare **16** *via* bis-trimethylsilylation of its unusually unstable[31] precursor, 2-biphenylylhydroxylamine.[32]

We note that while the thermal instability of **14a** under reaction conditions needed for Si_2Me_6 deoxygenation of **7a**



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precludes a search for residual **14a** expected from **7a** and Si_2Me_6 on the basis of eq 10, derivatives of **14** where R = alkyl and X = Me have been shown[25] to require fragmentation temperatures (~200°) which approach those presently reported (220–240°) for deoxygenation. Consequently, disilane deoxygenation studies with nitroalkanes, which we are pursuing, may lead to isolation of derivative compounds with structure **14** and thereby provide partial support for the heuristic mechanism represented by eq 10.

Unequivocal mechanistic conclusions, especially with regard to the question of nitrene intermediacy, are beyond the scope of the present exploratory study and a detailed interpretation of the variable product ratios listed in Table II would be premature. By way of a starting point and for the sake of simplicity we have assumed, nevertheless, that a nitrene intermediate is produced by disilane deoxygenation of **1** and that the relative proportion of **4** and **3** is qualitatively indicative of singlet and triplet participation, respectively, in the reaction manifold. The uniquely high percentage of triplet product **3** produced by Si_2Cl_6 (despite the absence of abstractable H atoms), relative to the organodisilanes, can be accounted for on the basis of a "heavy atom effect" associated with the chlorine nuclei in Si_2Cl_6. Such an effect could accelerate crossing of initially produced singlet **2** to triplet **2** by efficient intermolecular interactions immediately following nitrene generation (eq 10).[33]

To test the preceding hypothesis, deoxygenation of **1** with 2 molar equiv of **6**, which had produced the highest **4**:**3** ratio (71:1), was carried out (240°, 1.5 hr) in the presence of 4 molar equiv of CCl_4 as a potential heavy atom donor. Expectations for a CCl_4-induced increase in the relative proportion of **3** over **4** were confirmed by our finding that **4**:**3** = 1:35. Control reactions (see Experimental Section) demonstrated that this product ratio change was not due to selective decomposition of **4** by CCl_4.

If heavy atom effects associated with Si_2Cl_6 and CCl_4 do play a role in the deoxygenation of **1**, the inefficiency of ODCB and other aryl halides that we have used as solvents toward inducing similar effects is not understood.[33]

Attempted Photochemical Deoxygenations with Hexamethyldisilane. Ultraviolet absorption by nitroaromatics in the region of ~300 mμ is generally ascribed to an $n \rightarrow \pi^*$ transition which produces a short-lived photoexcited state.[36] The diradical character and increased reactivity expected for this excited state species is further believed to manifest itself in bimolecular photochemical transformations with a vaiety of reaction partners that are not observed under thermal conditions.[36] We have therefore explored the possibility of photoinduced NO_2 group reduction[37] with disilanes; however, results obtained with **1** and Si_2Me_6 as a model system were discouraging (see Experimental Section).

Conclusions

Aside from fundamental mechanistic questions which remain unanswered, the present results clearly demonstrate that deoxygenation of nitro compounds can be accomplished with disilane reagents. Our results also suggest that reaction temperatures necessary for these deoxygenations may severely limit practical applications earlier envisaged for this new method in organic synthesis. Development of more reactive disilanes to overcome this current restriction is in progress.

Experimental Section[38]

Preparation of Disilanes. Hexachlorodisilane was purchased from Alfa-Ventron and was used under anhydrous and oxygen-free conditions without further purification. The procedure of Wilson and Smith[13] afforded Si_2Me_6 containing ≤~5% contamination by Si_2OMe_6 and "xylenes" (vpc, column A, 60°, 60 ml/min). Purified Si_2Ph_6 was obtained (50%) by slow recrystallization (hot benzene) of crude material that was prepared (85%) according to literature directions.[39] Phenoxypentamethyldisilane[7] (bp ~60°, 1 mm) was synthesized from chloropentamethyldisilane[40] by analogy to standard procedures[41] and was purified by preparative vpc with column A (150°, 60 ml/min). Standard reaction of phenylmagnesium bromide with an equimolar amount of chloropentamethyldisilane gave crude $Si_2Me_5(Ph)$,[42] which was purified in the same manner as $Si_2Me_5(OPh)$. Compound **6** was synthesized according to procedures described elsewhere[17] and was purified[17] prior to use.

Nitro Compound Deoxygenation with Disilanes. General Procedures. Vpc scale reaction mixtures (~0.2–0.3 ml total volume) were sealed (*in vacuo*) in thick-walled Pyrex tubes before heating in a calibrated, preequilibrated, Büchi ("Kugelrohr") hot air bath furnace. Reaction mixtures which were heterogeneous at room temperature were found to be homogenous at temperatures (200–240°) required for reduction. Preparative scale reactions were run in the same manner as vpc scale studies using an appropriate number of glass tubes. *Caution:* in all cases a ratio of tube volume to liquid volume (at room temperature) of *ca.* 4–5 was used without incident, except for one spurious tube explosion with **1** and Si_2Me_6 in *o*-dichlorobenzene (ODCB). Additional details are reported in Tables I–III and under specific headings which follow.

Deoxygenation of 2-Nitrobiphenyl (1) with Si_2Me_6. Vacuum (0.3 mm) short-path distillation of a reaction mixture, which was obtained by heating **1** (50 mg, 0.25 mmol) and Si_2Me_6 (0.1 ml, 0.5 mmol) in ODCB at 240° for *ca.* 2 hr, led to isolation of an oil (fraction A, bp 50–100°) and a less volatile solid (fraction B, bp 100–140°). Tlc [silica gel PF-254, petroleum ether (bp 30–60°)–ether (90:10)] comparison with authentic materials indicated that fractions A and B were **3** and **4**, respectively. Thick-layer chromatography of fraction A, followed by recrystallization from ethanol, gave pure **3** (4 mg, 4%), mp 46°, which was positively identified by ir and vpc comparisons with genuine **3** (mp 47–48°) prepared from zinc reduction of **1** according to the method of Kuhn.[43] Recrystallization of fraction B from CH_2Cl_2–petroleum ether (bp 30–60°) yielded pure **4** (35 mg, 42%) with melting point, ir, and vpc characteristics identical with those of purified commercial material (mp 243°).

Quantitative vpc analysis (column A, 60°, 60 ml/min) of a duplicate reaction mixture indicated a *ca.* 90% yield of Si_2OMe_6, based on the amount of reacted **1** (86%). The latter quantity and corrected yields for **3** (8%) and **4** (68%) were determined by vpc (column D, 170°, 60 ml/min) after addition of triphenylmethane internal standard. Material balances in this and subsequent runs were between 80 and 90%; slow-eluting dark-colored "tars" were evident by tlc, and a minor (~1%) unidentified component eluted (vpc) between **1** and triphenylmethane.

Relative Disilane Deoxygenation Rates for 1. Solutions of **1** (0.7 *M*) with the various disilanes (1.4 *M*) listed in Table II were heated at 240 ± 5° for 1.5 hr according to the above general procedures. Quantitative vpc analyses (column D, 170°, 60 ml/min) for all of the organodisilanes were carried out after dissolution of solids in CH_2Cl_2 and addition of triphenylmethane internal standard; the presence of unreacted disilane was confirmed by vpc. In the case of Si_2Cl_6, vpc analysis of the reaction mixture was preceded by dilution with CH_2Cl_2 and then vigorous stirring with 20% aqueous potassium hydroxide solution. Control reactions demonstrated that **1**, **3**, and **4** are not effected by this hydrolysis procedure,[6a] which removed corrosive and highly reactive silicon-based compounds. Results are summarized in Table II. Vpc precision was judged to be *ca.* ±5% and duplicate runs with **1** and Si_2Me_6 gave *ca.* ±5% relative precision error for the yields of **3**, **4**, and unreacted **1**. Control studies with **1** and Si_2Me_6 demonstrated that doubling the usual tube volume:liquid volume ratio (*vide supra*) did not significantly effect the extent of reaction or the ratio of **3**:**4**.

Deoxygenation of Other Nitroaromatics with Si_2Me_6. Vpc analysis (column B, 100°, 60 ml/min) of a solution of nitrobenzene (**7a**) (0.2 ml, 2 mmol) in Si_2Me_6 (1.2 ml, 6 mmol) that was heated at 240° for 43 hr indicated a 1:1 ratio of **8a** and unreacted **7a**.

These vpc component identifications were confirmed by Kugelrohr distillation of the reaction mixture to give an oil (bp 30–150°, 160 mm) from which **8a** (22%) and **7a** (16%) were collected by preparative vpc (column C, 135°, 60 ml/min) for ir comparisons with genuine samples. Column chromatography [silica gel, petroleum ether (bp 30–60°) with increasing proportions of ether] of the distillation pot residue led to isolation (11%) and characterization of **9a** by ir comparison with commercial material. Heating at 1:3 molar mixture of **9a**:Si_2Me_6 under the above reaction conditions afforded recovered **9a** in 90% yield, and a similar control study with **8a** led to quantitative recovery (vpc) of unchanged **8a**.

Repetition of the above experiment (42 hr of heating) with freshly distilled **o-nitrotoluene (7b)** yielded (vpc, column B, 100°, 60 ml/min) 22% unchanged nitro starting material and 14% **8b** which was identified by its vpc retention time. Column chromatography (same as with **7a**) led to isolation of a trace quantity (<5%) of unidentified dark red colored crystals (mp >300°) and pale yellow colored crystals which rapidly decomposed.

The above procedures were carried out with ***p*-nitrotoluene (7c)** using a 45-hr heating period. Quantitative vpc analysis revealed 50% **7c** and approximately 30% **8c**, which eluted as a peak extensively overlapped with a lesser amount of an unknown component having a slightly longer retention time; isolation of this later material was not successful. Column chromatography of the reaction mixture gave a yellow-colored oil which crystallized from petroleum ether (bp 30–60°) as light orange colored crystals (mp 140°) that were identified as the thermodynamically more stable[44] *trans*-**9c** azo product (10%, lit.[44] mp 144°; lit.[44] mp 105° for *cis*-**9c**).

Deoxygenation of Azoxybenzene with Si_2Me_6. A mixture of recrystallized azoxybenzene (99 mg, 0.5 mmol) and Si_2Me_6 (0.3 ml, 1.5 mmol) was subjected to the same reaction conditions as those reported above for **7a**. Tlc analyses [silica gel PF-254, petroleum ether (bp 30–60°)–ether (90:10)] indicated that very little (if any) azoxy compound remained and that a major product was accompanied by at least three minor, strongly fluorescent, slower eluting components. The major reduction product was isolated by thick-layer chromatography and was identified by ir comparison with authentic material as **9a** (36 mg, 40%).

Kinetics for Si_2Me_6 Deoxygenation of 7a. Three sealed ampoules containing aliquots of a stock solution of **7a** (0.25 mmol) in Si_2Me_6 (1 ml, 5 mmol) containing ODCB (0.05 mmol) as a vpc internal standard were heated in a constant temperature oil bath which was preset and maintained at 220 ± 3°. Tube removal after 4, 19, and 31 hr was followed by duplicate vpc measurements of relative values for [**7a**] given by (area **7a**)/(area ODCB). A value for $\tau_{1/2} = 33.8$ hr ($k'_{220°} = 5.7 \times 10^{-6}$ sec^{-1}) was obtained from a plot of ln ($[\mathbf{7a}]_t/[\mathbf{7a}]_i$) *vs.* time, which was linear and passed through the origin. A duplicate kinetic run gave $\tau_{1/2} = 34.7$ hr ($k'_{220°} = 5.5 \times 10^{-6}$ sec^{-1}). Use of the average psuedo-first-order deoxygenation rate constant ($k'_{220°} = 5.6 \pm 0.1 \times 10^{-6}$ sec^{-1}) in the Erying equation gave $\Delta G^{\ddagger}_{220°} = 41$ kcal/mol.

Attempted Deoxygenation of 2-Nitrosobiphenyl (13). A solution of **13**[45] (0.17 *M*) and Si_2Me_6 (3.3 *M*) in ODCB was heated in the usual manner at 90° for 19 hr, as was a separate control sample of **13** (0.17 *M*) in ODCB. Tlc [silica gel PF-254, petroleum ether (bp 30–60°)–ether (90:10)] of both the reaction mixture and control sample gave essentially the same spectrum of components, which featured a spot having the same R_f value as **4** and indicated the presence of at least five additional components, plus residual "tars." Only a trace amount of **13** was apparently present and **3** was not detected. Thick-layer chromatographic (same conditions) isolation of the component initially thought to be **4** (mp 243°) gave a 10 w/w % yield of dark brown colored crystals (mp 148–151°) after crystallization from CH_2Cl_2–petroleum ether (bp 30–60°). Further characterization of this unknown product was not pursued, although it was found to have the same vpc retention time as authentic **4** (column D, 170°, 60 ml/min).

Deoxygenation of 1 with 6 in the Presence of CCl_4. A solution of **1** (1 *M*), **6** (2 *M*), and CCl_4 (4 *M*) in ODCB was heated in the usual manner at 240° for 1.5 hr. Quantitative vpc analysis (same as above, with triphenylmethane internal standard) indicated the presence of 33% unreacted **1** with 35% and 1% yields of **3** and **4**, respectively. Material loss of 32% was associated almost entirely with a reaction product that eluted shortly after **1** and could not be isolated in a pure state for further characterization. Heating **4** (0.04 mmol) and CCl_4 (0.22 mmol) in ODCB under the above reaction conditions led to an ~10% (vpc) loss of **4**, while a similar control experiment with **3** (0.05 mmol) and CCl_4 (0.22 mmol) led to an ~60% decrease in the concentration of **3**.

Pyrolysis of 14a in the Presence of 7a and Si_2Me_6. A 1:1:3 molar mixture of **14a**[25]:**7a**:Si_2Me_6 was simultaneously heated (23 hr, 240°) in the usual manner with a second tube containing a 1:3 molar mixture of **14a**:Si_2Me_6. Duplicate vpc analyses (column B, 170°, 120 ml/min) of each reaction mixture, using appropriate thermal conductivity correction factors, gave molar ratios of **8a**/**9a** = 1.3 and 3.7 for the three- and two-component mixtures, respectively. Heating a 1:3 molar mixture of **7a**:Si_2Me_6 under the above reaction conditions gave a value of **8a**/**9a** = 3.5, while a duplicate experiment with a 42-hr heating period gave a molar ratio for **8a**/**9a** = 2.5, which was more in accord with earlier data obtained with **7a** listed in Table III.

Attempted Photochemical Deoxygenations. Approximately 3-ml aliquots of a cyclohexane stock solution of **1** [0.05 *M*; λ_{max} (C_6H_{12}) 290 mμ (log ε 3.2)] which contained a fivefold molar excess of Si_2Me_6 and tetradecane as an internal vpc standard, were irradiated at 3000 Å in stoppered quartz tubes using a Rayonet photochemical reactor equipped with a "merri-go-round" apparatus. After 4 and 16 hr, vpc analyses (column B, 160°, 120 ml/min) revealed that the concentration of **1** decreased by ~5 and 20%, respectively, without detectable (vpc) formation of **3** or **4**. Repetition of the above experiments using solutions that did not contain Si_2Me_6 gave essentially the same results, within experimental error. Analogous data were obtained by use of 2537-Å light.

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Registry No.–**1**, 86-00-0; **3**, 90-41-5; **4**, 86-74-8; **7a**, 98-95-3; **7b**, 88-72-2; **7c**, 99-99-0; *trans*-**9c**, 21650-54-4; **13**, 21711-71-7; **14a**, 53783-47-4; azoxybenzene, 495-48-7.

References and Notes

(1) ACS–PRF Undergraduate Research Participant, 1973–1974.

(2) R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964), and original literature citations therein. See also R. A. Abramovitch and B. A. Davis, *J. Chem. Soc. C*, 119 (1968); C. Floriani and G. Fanchinetti, *J. Chem. Soc., Chem. Commun.*, 17 (1973); and E. Sappa and L. Milone, *J. Organometal. Chem.*, **61**, 383 (1973).

(3) (a) H. Alper and J. T. Edward, *Can. J. Chem.*, **48**, 1543 (1970); (b) J. M. Landesberg, L. Katz, and C. Olsen, *J. Org. Chem.*, **37**, 930 (1972); A. F. M. Iqbal, *Helv. Chim. Acta*, **55**, 798 (1972).

(4) (a) J. I. G. Cadogan and M. Cameron-Wood, *Proc. Chem. Soc., London*, 361 (1962); (b) J. I. G. Cadogan, *Quart. Rev., Chem. Soc.*, **22**, 222 (1968); (c) R. A. Abramovitch, B. A. Davis, and R. A. Brown, *J. Chem. Soc. C*, 1146 (1969); J. I. G. Cadogan, *Synthesis*, **1**, 11 (1969); R. J. Sundberg and G. S. Kotchman, Jr., *J. Org. Chem.*, **34**, 2285 (1969); J. I. G. Cadogan, *Accounts Chem. Res.*, **5**, 303 (1973); F. R. Atherton and R. W. Lambert, *J. Chem. Soc., Perkin Trans. 1*, 1079 (1973); D. E. Ames, K. J. Hansen, and N. D. Griffiths, *ibid.*, 2818 (1973); T. Kametani, F. F. Ebetino, and K. Fukumoto, *ibid.*, 861 (1974).

(5) (a) For a review with original literature citations thru 1967, see J. H. Boyer in "Nitrenes," W. Lwowski, Ed., Interscience, New York, N.Y., 1970, Chapter 5; (b) A. J. Boulton, I. J. Fletcher, and A. R. Katritzky, *Chem. Commun.*, 62 (1968); (c) J. I. G. Cadogan and M. J. Todd, *J. Chem. Soc. C*, 2808 (1969); (d) R. J. Sundberg, B. P. Das, and H. R. Smith, Jr., *J. Amer. Chem. Soc.*, **91**, 658 (1969); (e) R. J. Sundberg, R. H. Smith, Jr., and J. E. Bloor, *ibid.*, **91**, 3392 (1969); R. J. Sundberg and C. C. Lang, *J. Org. Chem.*, **36**, 300 (1971); R. A. Abramovitch, J. Court, and E. P. Kyba, *Tetrahedron Lett.*, 4059 (1972); P. K. Broske, R. B. Herbert, and F. G. Holliman, *ibid.*, 761 (1973).

(6) (a) K. Naumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7012 (1969); (b) *ibid.*, **91**, 2788 (1969); T. J. Katz, J. C. Carnahan, Jr., G. M. Clarke, and N. Acton, *ibid.*, **92**, 734 (1970); D. K. Meyers and L. D. Quinn, *J. Org. Chem.*, **36**, 1285 (1971); (c) J. P. Synder, L. Lee, V. T. Bandurco, C. Y. Yu, and R. J. Boyd, *J. Amer. Chem. Soc.*, **94**, 3260 (1972).

(7) H. Sakurai, M. Kira, and M. Kumada, *Bull. Chem. Soc. Jap.*, **44**, 1167 (1971).

(8) L. Spialter and J. D. Austin, *J. Amer. Chem. Soc.*, **88**, 1828 (1966); *Inorg. Chem.*, **5**, 1975 (1966).

(9) Reductive coupling of nitrobenzene by diphenylsilane in the presence of potassium trimethylsilanolate to yield azobenzene has been recently reported, but no evidence for disilane involvement was presented: K. A. Andrianov, L. M. Tartakovskaya, and B. I. Shapiro, *Zh. Obshch. Khim.*, **42**, 176 (1972).

(10) See also W. E. Krueger and J. R. Maloney, *J. Org. Chem.*, **38**, 4208 (1973).

(11) D. J. H. Smith in "Organophosphorus Chemistry," Vol. 4, S. Trippett, Ed., The Chemical Society, Burlington House, London, 1974, Chapter 1.

(12) An earlier report (ref 6a, footnote 47) that nitrobenzene is not reduced by hexachlorodisilane (Si_2Cl_6) in refluxing benzene is understandable in view of the present findings, *vide infra*.

(13) G. R. Wilson and A. G. Smith, *J. Org. Chem.*, **26**, 557 (1961).
(14) H. C. Waterman and D. L. Vivian, *J. Org. Chem.*, **14**, 289 (1949).
(15) F. D. Lewis and W. H. Saunders, Jr., in "Nitrenes," W. Lwowski, Ed., Interscience, New York, N.Y., 1970, Chapter 3, and original literature references cited therein.
(16) G. Zon, unpublished observations.
(17) A preliminary report on the synthesis and reactivity of **6** has been published: F. P. Tsui and G. Zon, *J. Organometal. Chem.*, **70**, C3 (1974).
(18) Although our present mechanistic understanding of disilane deoxygenations of nitro compounds is admittedly superficial (*vide infra*), we believe it reasonable to associate the sluggish reactivity of Si_2Ph_6 with extraordinary rate-retarding steric effects at some point along the reaction coordinate.
(19) M. Kumada, K. Tamao, T. Takubo, and M. Ishikawa, *J. Organometal. Chem.*, **9**, 43 (1967); V. Yu. Orlov, L. E. Gusel'nikov, N. S. Nametkin, and R. L. Ushakova, *Org. Mass Spectrom.*, **6**, 309 (1972).
(20) R. E. Smith, *Trans. Faraday Soc.*, **36**, 983 (1940); Y. Y. Maksimov, *Teor. Vzryvchatykh Veshchestv*, 338 (1963) [*Chem. Abstr.*, **59**, 15137*a* (1963)].
(21) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **89**, 724 (1967); *ibid.*, **89**, 3224 (1967).
(22) V. I. Zetkin, *et al.*, *Z. Fiz. Khim.*, **41**, 895 (1967) [*Chem. Abstr.*, **67**, 63544j (1967)].
(23) H. Sakurai, T. Imoto, N. Hayashi, and M. Kumada, *J. Amer. Chem. Soc.*, **87**, 4001 (1965).
(24) The intermediacy of **13** in a chemically excited state having increased oxidative reactivity toward Si_2Me_6 cannot be excluded on the basis of our data and remains as a viable option.
(25) F. P. Tsui, T. M. Vogel, and G. Zon, *J. Amer. Chem. Soc.*, **96**, 7144 (1974).
(26) Analogous α-elimination of alkoxysilanes in systems which yield carbenes[27] (R_2C:) and silylenes[28] (R_2Si:) has been reported.
(27) W. H. Atwell, D. R. Weyenberg, and J. G. Uhlmann, *J. Amer. Chem. Soc.*, **91**, 2025 (1969); A. G. Brook and P. J. Dillon, *Can. J. Chem.*, **47**, 4347 (1969).
(28) W. H. Atwell and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **90**, 3438 (1968); *J. Organometal. Chem.*, **5**, 594 (1966).
(29) Formation of azoxy compounds from reaction of aryl nitroso compounds with phosphorus reagents *via* addition of derived arylnitrenes to unreacted nitroso starting material has been discussed.[4b]
(30) A control reaction (see Experimental Section) demonstrated that azoxybenzene [PhN=N(O)Ph] undergoes complete reaction with a threefold molar excess of Si_2Me_6 at 240° to yield **9a**.
(31) T. B. Patrick, J. A. Schield, and D. G. Kirchner, *J. Org. Chem.*, **39**, 1758 (1974).
(32) T. M. Vogel and G. Zon, unpublished work.
(33) Acceleration of singlet → triplet crossing by heavy atom solvents has been reported[34] for cyanonitrene; however, the complexity of such intermolecular interactions has been revealed by more recent studies[35] leading to consideration of heavy atom solvent deceleration of this nitrene intersystem crossing.
(34) A. G. Anastassiou *J. Amer. Chem. Soc.*, **89**, 3184 (1967).
(35) R. Gleiter and R. Hoffmann, *Tetrahedron*, **24**, 5899 (1968); G. R. Felt, S. Linke, and W. Lwowski, *Tetrahedron Lett.*, 2037 (1972); D. S. Breslow and E. I. Edwards, *ibid.*, 2041 (1972).
(36) H. A. Morrison in "The Chemistry of the Nitro and Nitroso Groups," Part 1, H. Feuer, Ed., Interscience, New York, N.Y., 1969, Chapter 4, and original literature citations therein.
(37) R. J. Sundberg and R. H. Smith, Jr., *J. Org. Chem.*, **39**, 93 (1974); E. C. Taylor and E. E. Garcia, *ibid.*, **30**, 655 (1965); R. Obrycki and C. E. Griffin, *ibid.*, **33**, 632 (1968).
(38) Nmr spectra were recorded on a Varian A-60 spectrometer at ambient probe temperature, using *ca.* 10 v/v % solutions in deuteriochloroform and tetramethylsilane as an internal reference. Ir and uv measurements were carried out with Perkin-Elmer Model 137 and Cary Model 15 spectrometers, respectively. A Varian Aerograph Model 920 thermal conductivity gas chromatograph was used for vpc studies; quantitative measurements utilized either predetermined thermal conductivity correction factors or addition of authentic material with an internal reference. Vpc columns were made of standard 0.25 in. aluminum or stainless steel tubing and include column A = 6 ft, 15% Apiezon L on Chromosorb W, 60–80 mesh; column B = 3 ft, 5% SE-30 on Chromosorb G, 60–80 mesh; column C = 6 ft, 15% SE-30 on Chromosorb G, 60–80 mesh; column D = 5 ft, 3% SE-30 on Varaport 30, 100–120 mesh (Varian Aerograph). All melting point and boiling point data are uncorrected.
(39) H. Gilman and G. E. Dunn, *J. Amer. Chem. Soc.*, **73**, 5077 (1951).
(40) H. Sakurai, K. Tominaga, T. Watanabe, and M. Kumada, *Tetrahedron Lett.*, 5493 (1966).
(41) G. Schott and V. Bondybey, *Chem. Ber.*, **100**, 1773 (1967).
(42) R. Calas, A. Marchand, E. Frainnet, and P. Gerval, *Bull. Soc. Chim. Fr.*, 2478 (1968).
(43) W. E. Kuhn, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N.Y., 1943, p 447.
(44) A. H. Cook, *J. Chem. Soc.*, 876 (1938).
(45) Compound **13** was prepared by the method of Yost and Gutman[46] after repeated failure was encountered with attempts to employ the standard procedure of W. J. Mijs, S. E. Heckstra, R. M. Uhlmann, and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **77**, 746 (1958).
(46) Y. Yost and H. R. Gutmann, *J. Chem. Soc. C*, 2497 (1970).

Dihydrophenophosphazine Ring System[1]

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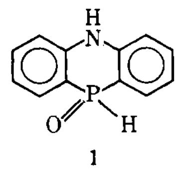
The reaction of diarylamines with phosphorus trichloride followed by treatment of the reaction mixtures with water has been employed to synthesize the secondary phosphine oxides **1**, **3**, **5**, and **7** and the spirophosphonium chlorides **2**, **4**, **6**, and **8**. A mechanism for the formation of the oxides has been proposed. Phosphinic acids have been prepared by oxidation of the oxides. The *N*-methyl derivative **12** has been obtained by a variant of the Friedel-Crafts reaction in which *N*-methyl-di-*p*-tolylamine and phosphorus trichloride were heated together in the presence of aluminum chloride and the reaction mixture was then hydrolyzed and oxidized.

It has long been known that the reaction of diphenylamine with phosphorus trichloride followed by treatment of the reaction mixture with water yields a heterocyclic phosphorus compound with the empirical formula $C_{12}H_{10}NOP$.[2] In 1960 Häring[3] published detailed directions for this reaction and showed that the heterocyclic compound is a secondary phosphine oxide, viz. 5,10-dihydrophenophosphazine 10-oxide (**1**). On attempting to repeat Häring's method of preparation, we found[4] that the phosphine oxide **1** was invariably admixed with a chlorine-containing compound $C_{24}H_{18}ClN_2P$. The chemical and spectral properties of the latter substance showed that it did not contain a P–H bond and that it was not a derivative of trivalent phosphorus. The structure of the unknown substance was unambiguously shown by an X-ray study[4,5] to be 10,10′(5*H*,5′*H*)-spirobiphenophosphazinium chloride (**2**). This was the first spirophosphonium compound re-



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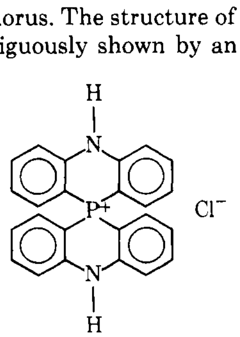

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