

A STUDY OF THE SYNTHESIS OF SOME
ALUMINUM AND PHOSPHORUS
DERIVATIVES OF ALKYL
HYDRAZINES

By
ROBERT PETER NIELSEN

A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

June, 1962

ACKNOWLEDGMENTS

The author wishes to acknowledge the friendly cooperation of his committee and the faculty of the Chemistry Department of the University of Florida. It is considered both an honor and an opportunity to have worked under the direction of Dr. Harry H. Sisler, who, although entrusted with the momentous task of administration of this Department, is able to give generously of his time and abilities to direct meaningful scientific inquiry. His friendship and wide scope of interests have proved inspiring.

The time and effort spent by Commander N. L. Smith (Ret. USNR) in acquainting the author with synthetic technique and phosphorus-nitrogen chemistry is sincerely appreciated. Besides offering an open door and a sympathetic ear, he provided encouragement when it was needed and advice when it was desired.

Thanks go also to Dr. Wallace Brey and Mr. Ken Lawson for nuclear magnetic resonance measurements, and Mr. Howard Latz and Mr. Leo Pijanowski for assistance in obtaining infrared spectra. The fellow members of the Inorganic Section deserve thanks for friendly competitive spirit and helpful discussion.

The author is indebted to the Petroleum Research Fund for a financial grant which made this work possible.

TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	ii
LIST OF TABLES	iv
LIST OF FIGURES	vi
Chapters	
I	
THE INTERACTION OF TWO ALKYL HYDRAZINES WITH TRIETHYLALUMINUM	1
Introduction	1
Experimental and Results	9
Discussion	27
Conclusion	35
II	
REACTIONS OF ARYLHALOPHOSPHINES AND DERIVATIVES OF ARYLHALOPHOSPHINES WITH SEVERAL ALKYL HYDRAZINES	36
Introduction	36
Experimental and Results	61
Discussion	123
Conclusion	147
BIBLIOGRAPHY	149
BIOGRAPHICAL SKETCH	153

LIST OF TABLES

Table		Page
1	Amine Alanes	5
2	Bis-Amine Alanes	6
3	Bis-(Mixed) amine Alanes	6
4	Inner Complex Amine Alanes	6
5	Aminoalanes	7
6	Extended Network Aluminum-Nitrogen Polymers	8
7	Hydrazine Alanes	8
8	Hydrazinoalanes	8
9	Hydrazinoalane-Hydrazine Adducts	9
10	Polymeric Species	9
11	Alkyl and Aryl Phosphorohydrazidates	39
12	Alkyl and Aryl Phosphorohydrazidothioates	40
13	Alkyl and Aryl Phosphorophenylhydrazidothioates	42
14	Phenylhydrazidoalkylphosphonates	43
15	Bis(hydrazino)phenylphosphine Oxides	44
16	Arylphosphorodihydrazidothioates	45
17	Tris(hydrazino)phosphine Oxides and Sulfides	47
18	Arylphosphorochloridohydrazidothioates	48
19	Alkylphosphorohydrazidoic Acids	49
20	Arylphosphoroamidohydrazidothioates	50
21	Amino-bis(hydrazino)phosphine Oxides	54
22	Amino-bis(hydrazino)phosphine Sulfides	55
23	Salts of Phosphorohydrazidates	56

LIST OF TABLES Continued

Table		Page
24	Benzylidene Derivatives of Alkylphosphorohydrazidates	58
25	Hydrazones of Bis(hydrazino)phenylphosphine Oxides-Hydrazones of Bis(hydrazino)phenylphosphine Sulfides	59
26	Principal Infrared Absorption Frequencies for Some Phosphorus Hydrazine Derivatives	124
27	Infrared Absorption Frequencies and Assignments	125
28	Nuclear Magnetic Resonance Data Summary	128
29	Scale of Chemical Shift Values from N. M. R. Data	133

LIST OF FIGURES

Figure		Page
1	Mini-Lab Distillation Apparatus	12
2	Reaction Apparatus	13
3	Molecular Weight Apparatus (Modified for Atmosphere-Sensitive Compounds)	14
4	Infrared Spectrum of 2,2-Dimethylhydrazinodiethylalane (Melt)	18
5	Infrared Spectrum of 2,2-Dimethylhydrazinodiethylalane (Dilute Hexane Solution)	19
6	Infrared Spectrum of Condensation Product, $(EtAlNMe_2)_x$ (Hexane Solution)	22
7	Mini-Lab Reaction Apparatus	63
8	Dry Box (Three-eighths Inch Lucite Construction)	64
9	Infrared Spectrum of 2,2-Dimethylhydrazinodiphenylphosphine (Nujol Mull)	67
10	Proton Nuclear Magnetic Resonance Spectrum of 2,2-Dimethylhydrazinodiphenylphosphine	68
11	Infrared Spectrum of 2,2-Dimethylhydrazinodiphenylphosphine Oxide (Nujol Mull)	71
12	Infrared Spectrum of 2,2-Dimethylhydrazinodiphenylphosphine Sulfide (Nujol Mull)	73
13	Infrared Spectrum of 2,2-Dimethylhydrazinomethyl-diphenylphosphonium Iodide (Nujol Mull)	75
14	Infrared Spectrum of 1,1-Bis(diphenylphosphino)-2,2-dimethylhydrazine (Nujol Mull)	81
15	Infrared Spectrum of the Product of the Reaction of 2,2-Dimethylhydrazinodiphenylphosphine and Carbon Disulfide (Nujol Mull)	85
16	Infrared Spectrum of Diphenylphosphine (Cell)	90

LIST OF FIGURES Continued

Figure		Page
17	Infrared Spectrum of 1,1,2-Tris(diphenylphosphino)-methylhydrazine (Nujol Mull)	93
18	Infrared Spectrum of 1,2,2-Trimethylhydrazino-diphenylphosphine Oxide (Nujol Mull)	96
19	Infrared Spectrum of 1-Ethyl-2,2-dimethylhydrazino-diphenylphosphine Sulfide (Nujol Mull)	101
20	Infrared Spectrum of 1-Ethyl-2,2-dimethylhydrazino-diphenylphosphine Oxide (Nujol Mull)	104
21	Infrared Spectrum of 1,2-Bis(diphenylphosphino)-hydrazine. (Nujol Mull)	107
22	Infrared Spectrum of Bis(2,2-dimethylhydrazino)-phenylphosphine (Nujol Mull)	110
23	Infrared Spectrum of Bis(2,2-dimethylhydrazino)-phenylphosphine Oxide (Nujol Mull)	113
24	Infrared Spectrum of Bis(2,2-dimethylhydrazino)phenylphosphine Sulfide (Nujol Mull)	116
25	Infrared Spectrum of Phosphoryl Tri(2,2-dimethylhydrazide) (Nujol Mull)	119
26	Infrared Spectrum of Thiophosphoryl Tri(2,2-dimethylhydrazide) (Nujol Mull)	121

CHAPTER I
THE INTERACTION OF TWO ALKYL HYDRAZINES
WITH TRIETHYLALUMINUM

Introduction

The highly interesting and challenging field of organometallic chemistry has undergone tremendous growth in recent years, and among other valuable contributions to the science of chemistry there have been discovered new modes of chemical combination, entirely new types of chemical compounds, new useful materials at lower costs than previously-used synthetics, and new routes to known materials.

Evidence of great interest in the field of organometallics manifests itself in the recent appearance of several texts devoted to this unique combination of organic and inorganic chemistry (1-4).

One of the areas of organometallic chemistry which has interested investigators for as long as metal alkyls have been known is the preparation and study of molecular addition complexes between the metal alkyls and various Lewis bases (electron pair donor compounds). The metals in which most interest has been shown are those of Group III of the Periodic System. Review articles covering various such molecular addition complexes have appeared over the years (5-11), but none of these articles is concerned exclusively with nitrogen complexes of aluminum, although aluminum-nitrogen complexes have been mentioned (12).

The reason that the many nitrogen-base complexes of aluminum alkyls and the various other alanes have not been the subject of an extended review article is that work on this group of compounds was begun in earnest only within the past few years. The importance of such compounds at this point seems to lie in their intrinsic properties as well as the fact that they are intermediates in condensation reactions. The aluminum-nitrogen compounds in which this great interest has been demonstrated may someday find application as high temperature polymeric materials and perhaps as propulsion fuels. As intermediates to new and exotic compounds they are virtually unexplored.

Well-established chemical and physical evidence concerning the nature of various alanes, and specifically the aluminum alkyls, indicate that they act as electron pair acceptors, or Lewis acids. The acceptor tendency is so great as to preclude their existence in the unassociated state (1,2). This fact provides a basis for the observed reluctance of investigators to use the Grignard method for preparing aluminum alkyls, since the compounds prepared can with only very great effort be freed of the ether used in the synthesis (13). The diethyl etherate of triethylaluminum has been studied in detail (13-15). The dimethyl etherate of trimethylaluminum has been found to be an extremely stable compound, so stable in fact that no dissociation data can be obtained in the gas phase (16); such data have been obtained for many other Group III addition complexes, however.

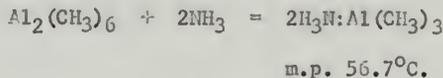
Various methods of preparation of molecular addition complexes of aluminum alkyls have been used, but the most common include direct combination in the vapor phase (both diluted and undiluted), direct combination in the liquid phase, and direct combination in a suitable

solvent. Some experiments have been carried out in which one (or both) of the reactants were generated in situ.

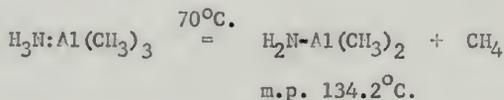
Since this work is concerned with nitrogen derivatives of aluminum it is appropriate to discuss those reactions and compounds reported in the literature which include aluminum-nitrogen molecular addition complexes and the aluminum-nitrogen covalent bond.

At this writing there have been reported in the literature three main types of covalently bonded aluminum--nitrogen compounds: the amine-alanes, the aminoalanes, and polymeric materials which contain aluminum-nitrogen bonds. These three types of compounds are intimately related and may be arranged in a reaction sequence where the initial molecular addition complex is the parent compound in a pyrolytic series, as in the following example: (17,18)

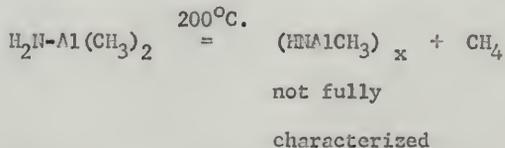
1. Adduct Formation of an Amine Alane.



2. Condensation to an Aminoalane.



3. Further Condensation to Polymeric Material.



4. High Temperature Pyrolysis to Extended Polymer.



A systematic investigation of systems of this nature has recently been carried out and the scope of the reaction has been extended to include many amines and several alanes (17). Examples of compounds of this type (excluding those shown above) are given in Tables 1-10, pages 5-9.

Reactions of these compounds other than by hydrolysis and condensation are largely unknown, and to date there is no mention in the literature of a useful polymer in the aluminum-nitrogen system. Various theoretical aspects of aluminum chemistry have been demonstrated, however, and no tendency for pi-bond formation between aluminum and nitrogen has been found.

Logical extensions to this work with alanes seem to lie in two directions: 1) Lewis bases can be used which contain functional groups other than and in addition to an amino group, and 2) polynuclear Lewis bases can be used.

The first of these alternatives has been explored in a very perfunctory manner and involves the reactions of alanes with olefinic amines, ethers, and thioethers to give various ring compounds and organic derivatives (19). Obvious possible uses for these reactions and intermediates lie in the field of polymerization catalysts.

The use of polynuclear Lewis bases with alanes was, until very recently, totally unexplored. Within the last year, however, there have appeared two articles concerning the interactions of aluminum alkyls with hydrazine and alkyl hydrazines (20, 21). It is interesting to note that the experimental results obtained by these workers are in most aspects in accord with the results we have recently obtained

TABLE 1
Amine Alanes

Compound	m.p.	b.p.	References
$(\text{CH}_3)_3\text{N}:\text{AlH}_3$	76°C.	----	22-24
$(\text{CH}_3)_3\text{N}:\text{AlD}_3$	77-78°C.	----	22
$(\text{C}_2\text{H}_5)_3\text{N}:\text{AlH}_3$	18-19°C.	----	22
$(\text{C}_3\text{H}_7)_3\text{N}:\text{AlH}_3$	80-81°C.	----	22
$\text{H}_3\text{CN}(\text{C}_2\text{H}_5)_2:\text{AlH}_3$	----	----	22
$\text{H}_2\text{C}=\text{CHCH}_2\text{N}(\text{CH}_3)_2:\text{AlH}_3$	12°C.	----	22
$(\text{CH}_3)_3\text{N}:\text{Al}(\text{CH}_3)_2\text{H}_2$	-35°C.	25°/1 mm.	25
$(\text{CH}_3)_3\text{N}:\text{Al}(\text{C}_2\text{H}_5)_2\text{H}_2$	----	39°/1 mm.	25
$(\text{CH}_3)_3\text{N}:\text{Al}(\text{CH}_3)_2\text{H}$	----	42°/1 mm.	25
$(\text{CH}_3)_3\text{N}:\text{Al}(\text{C}_2\text{H}_5)_2\text{H}$	-28°C.	63°/1 mm.	25
$(\text{CH}_3)_2\text{NH}:\text{Al}(\text{CH}_3)_3$	51°C.	186°C.	16
$(\text{CH}_3)_3\text{N}:\text{Al}(\text{CH}_3)_3$	105°C.	177°C.	16
$(\text{CH}_3)_3\text{N}:\text{Al}(\text{CH}_3)_2\text{Cl}$	124°C.	----	16
$(\text{CH}_3)_3\text{N}:\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	-5°C.	----	17
$\text{H}_3\text{CNH}_2:\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	-11.5°C.	----	17
$\text{H}_3\text{CNH}_2:\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$	15°C.	----	26
$\text{H}_3\text{N}:\text{Al}(\text{C}_6\text{H}_4\text{CH}_3)_3$	----	----	26
$\text{H}_3\text{N}:\text{Al}(\text{C}_6\text{H}_5)_3$	----	----	26

TABLE 2
Bis-Amine Alanes

Compound	m.p.	b.p.	References
$[(\text{CH}_3)_3\text{N}]_2:\text{AlH}_3$	95°C. d.	----	23,27,28
$[(\text{C}_2\text{H}_5)_3\text{N}]_2:\text{AlH}_3$	----	----	28
$[(\text{C}_2\text{H}_5)_2\text{NCH}_3]_2:\text{AlH}_3$	----	----	28
$[(\text{C}_3\text{H}_7)_3\text{N}]_2:\text{AlH}_3$	----	----	28
$[\text{CH}_2=\text{CHCH}_2\text{N}(\text{CH}_3)_2]_2:\text{AlH}_3$	----	----	28

TABLE 3
Bis- (Mixed) amine Alanes

Compound	m.p.	b.p.	References
$(\text{CH}_3)_3\text{N}(\text{C}_3\text{H}_7)_3\text{N}:\text{AlH}_3$	----	----	28
$(\text{CH}_3)_3\text{N}(\text{C}_2\text{H}_5)_3\text{N}:\text{AlH}_3$	----	----	28
$\text{H}_3\text{C}(\text{C}_2\text{H}_5)_2\text{N}(\text{H}_3\text{C})_3\text{N}:\text{AlH}_3$	----	----	28

TABLE 4
Inner Complex Amine Alanes

Compound	m.p.	b.p.	References
	----	115-116°C./1.5 mm.	19

TABLE 5
Aminoalanes

Compound	m. p.	b. p.	References
$[(\text{CH}_3)_2\text{N}-\text{Al}(\text{CH}_3)_2]_2$	154-156°C.	----	16
$[(\text{CH}_3)_2\text{N}-\text{AlH}_2]_3$	98- 90°C.	----	22
$[(\text{C}_2\text{H}_5)_2\text{N}-\text{AlH}_2]_2$	42°C.	----	22
$\{[(\text{CH}_3)_2\text{CH}]_2\text{N}-\text{AlH}_2\}_{2.16}$	130-131°C.	----	29
$[\text{CH}_3\text{NH}-\text{Al}(\text{C}_2\text{H}_5)\text{Cl}]_n$	91°C.	----	17
$[(\text{C}_2\text{H}_5)_2\text{N}-\text{Al}(\text{C}_2\text{H}_5)_2]_n$	----	141-145°C./14 mm.	19
$[(\text{CH}_3)_2\text{NA}(\text{C}_2\text{H}_5)\text{Cl}]_n$	80- 81°C.	----	17
$[(\text{CH}_3)\text{NH}-\text{AlCl}_2]_n$	90-104°C.	----	17
$[(\text{CH}_3)_2\text{NA}(\text{Cl})_2]_{2.4}$	----	----	17,29
<u>BIS-</u>			
$\{[(\text{CH}_3)_2\text{N}]_2\text{AlH}\}_{2.5}$	63°C.	----	24,29
$\{[(\text{CH}_3)_2\text{N}]_2\text{AlCl}\}_2$	55- 57°C.	----	29
$\{[(\text{CH}_3)_2\text{CH}]_2\text{NA}(\text{HN}(\text{CH}_3)_2)\}_2$	----	----	29
<u>TRIS-</u>			
$[(\text{CH}_3)_2\text{N}_3\text{Al}]_{2.2}$	87- 89°C.	----	24,29
$\{[(\text{CH}_3)_2\text{CH}]_2\text{N}\}_3\text{Al}$	58- 59°C.	----	29

TABLE 6
Extended Network Aluminum-Nitrogen Polymers

Compound	m.p.	b.p.	References
$[(\text{CH}_3)_2\text{NAlCl}]_n$	----	----	17
$(\text{AlN})_n$	above 220°C.	----	18,30

TABLE 7
Hydrazine Alanes

Compound	m.p.	b.p.	References
$(\text{CH}_3)_2\text{N-N}(\text{CH}_3)_2:\text{Al}(\text{CH}_3)_3$	80 -83 °C.	----	21
$(\text{CH}_3)_2\text{N-NHCH}_3:\text{Al}(\text{CH}_3)_3$	65.5-66.0°C.	----	21

TABLE 8
Hydrazinoalanes

Compound	m.p.	b.p.	References
$[(\text{CH}_3)_2\text{N-NH-Al}(\text{CH}_3)_2]_2$	77.0-78.5°C.	----	21
$[(\text{CH}_3)_2\text{N-N}(\text{CH}_3)-\text{Al}(\text{CH}_3)_2]_2$	125.0-126.5°C.	----	21
$[(\text{CH}_3)_2\text{Al-NH-NH-Al}(\text{CH}_3)_2]$	shock sensitive	----	20

TABLE 9
Hydrazinoalane-Hydrazine Adducts

Compound	m.p.	b.p.	References
$\text{H}_2\text{N-N}(\text{CH}_3)_2 : (\text{CH}_3)_2\text{Al-NH-N}(\text{CH}_3)$	31.0-32.0°C.	----	21

TABLE 10
Polymeric Species

Compound	m.p.	b.p.	References
$(\text{H}_3\text{CAINHNCH}_3)_n$	200°C. d.	----	21
$[\text{Al}(\text{NCH}_3\text{-NCH}_3)_3]_n$	----	----	21

independently at the University of Florida. Fortunately, there has been no duplication of effort since our work is concerned with triethylaluminum and the studies reported in the literature were made with other aluminum alkyls.

Experimental and Results

The following procedure was found to be very satisfactory for studying the interaction of triethylaluminum with 1,1-dimethylhydrazine and monomethylhydrazine.

Materials. 1,1-Dimethylhydrazine is commercially available and was distilled prior to using. The material used had a boiling range of 62.2-63.0°C./758 mm. Distillation was carried out over calcium hydride to remove any traces of water which the commercial material may have contained. Care was taken to observe completely anhydrous conditions during the transfer and handling of this and the other reagents and solvents used.

Triethylaluminum was purchased in 250 gram quantities in steel lecture bottles which were fitted with Teflon-packed needle valves. The purity of this material was not high enough to permit use without purification. Distillation at 56°C./0.50 mm. provided samples which analyzed 99.6 per cent triethylaluminum, as determined by measuring the ethane evolved upon aqueous hydrolysis.

Analytical Reagent grade solvents were distilled over calcium hydride prior to using and were then stored in air-tight glass containers with metal foil or polyethylene closure liners. All transfers were performed either in a dry box or by pipette with a nitrogen flush.

High purity nitrogen was used in the dry box and wherever a constant flush seemed necessary to avoid contact with the atmosphere.

Equipment. A dry box is essential in carrying out synthetic work with triethylaluminum and this piece of equipment is described in detail in Chapter II of this dissertation, under the Equipment section.

Distillations were carried out in Mini-Lab Standard Taper 14/20 apparatus as shown in Figure 1. The actual reactions were carried out in a Standard Taper 14/20 100 ml. round bottom flask fitted with two 10 mm. diameter by 30 mm. length side arms. Figure 2

illustrates this flask and the complementary equipment, which includes a pressure-equalizing addition funnel of 50 ml. capacity and a Precision Wet Test Meter. The Wet Test Meter can be read directly to the nearest 3 ml.

A freezing point depression type apparatus was used for molecular weight determinations. Its design was modified slightly in order to provide a constant, slow nitrogen flush so that contact of the solution with atmospheric oxygen could be avoided, as shown in Figure 3.

Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tennessee. Carbon, hydrogen, and nitrogen were estimated by combustion methods and special precautions were observed to maintain sample integrity before combustion.

Aluminum analyses were performed by the method of Schwarzenbach (31) in which the aluminum-containing solution is treated with excess disodium ethylenediaminetetraacetate and the excess titrated with standard zinc sulfate solution to the pink Eriochrome Black T end point.

The interaction of triethylaluminum with 1,1-dimethylhydrazine

In a typical experiment 8.0321 grams (0.0704 mole) triethylaluminum was vacuum distilled into a 100 ml. Standard Taper 14/20 round bottom flask fitted with two side arms and which contained a small, Teflon-encapsulated, magnetic stirring bar. All ground glass joints were lubricated with Kel-F fluorocarbon grease, which was found to be more resistant to attack by triethylaluminum than are other, more conventional stopcock greases, including silicone grease.

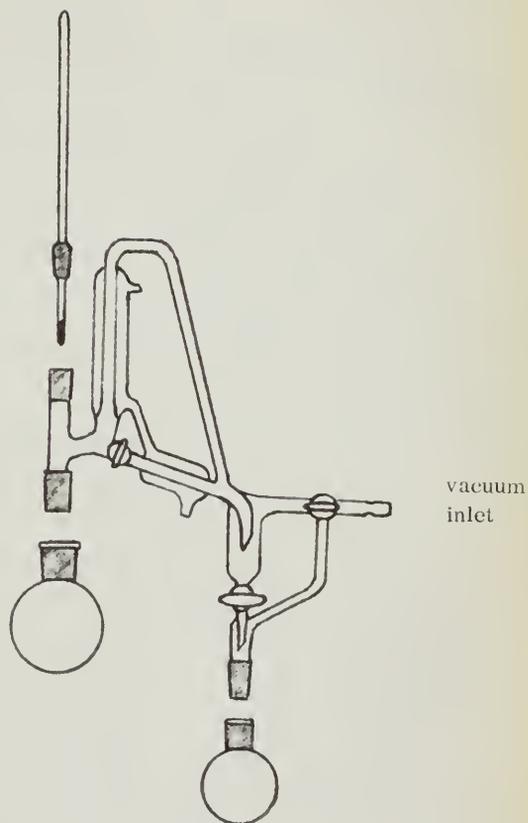
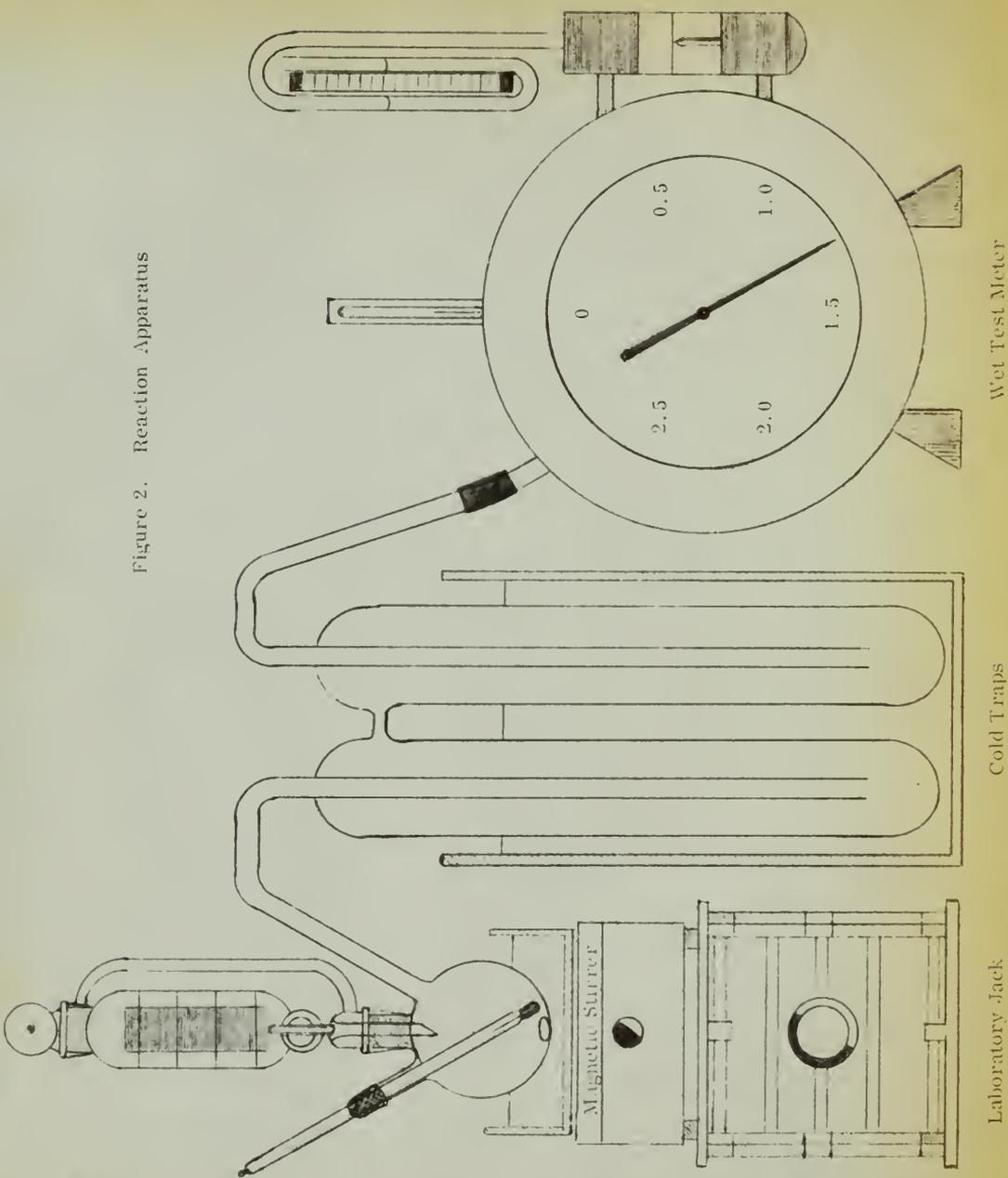
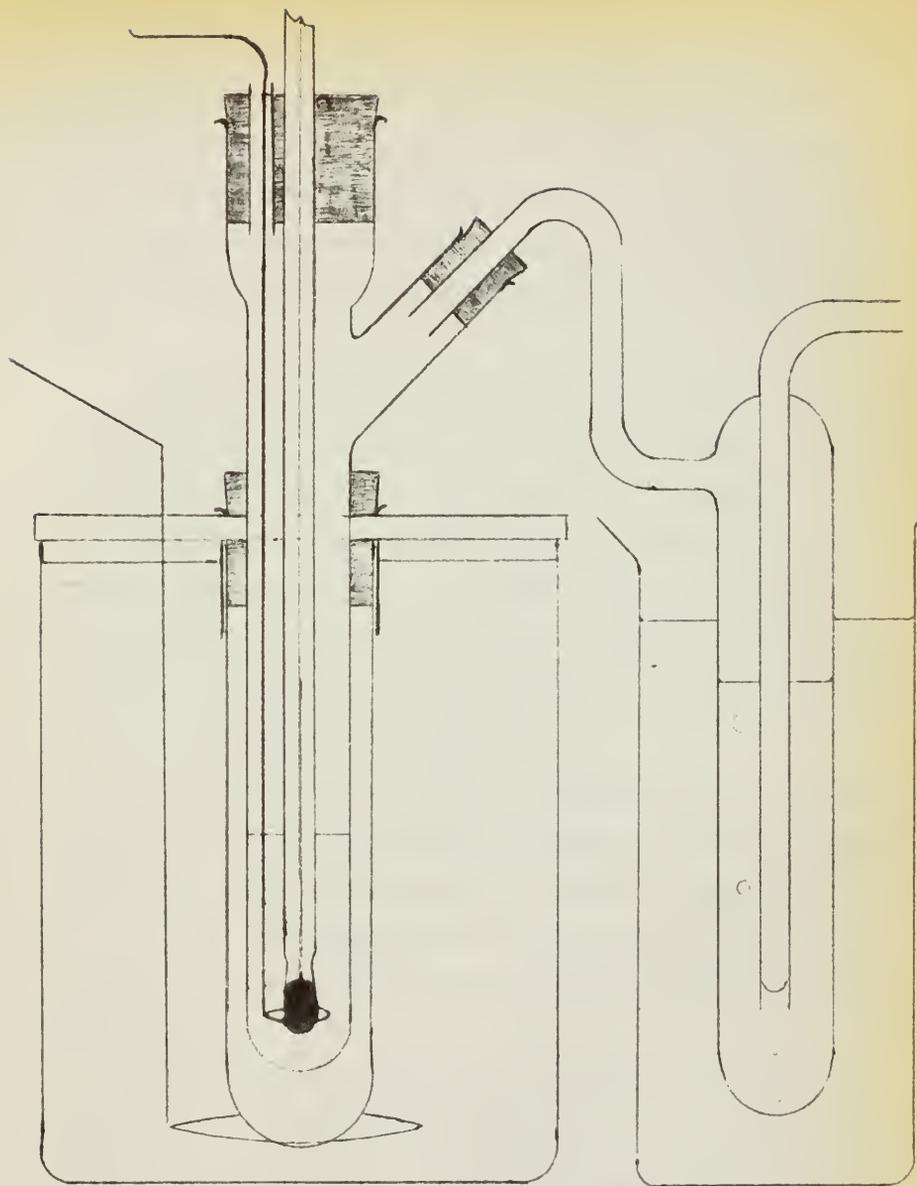


Figure 1. Mini-Lab Distillation Apparatus

Figure 2. Reaction Apparatus





Freezing Point Depression Apparatus

Solvent Bubble
(for saturating dry nitrogen)

Fig. 3. Molecular Weight Apparatus Modified for Atmosphere-Sensitive Compound

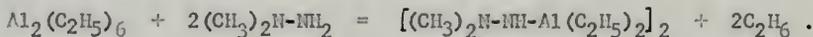
The triethylaluminum was frozen by immersing the lower half of the flask in a dry ice-acetone slurry. While a nitrogen flush was maintained above and around the flask, the stoppers which capped the side arms during distillation were removed and through one side arm was inserted a low range (to $-100^{\circ}\text{C}.$) pentane thermometer. The other side arm was connected via two dry ice-acetone traps to the Wet Test Meter.

The addition funnel, containing 4.44 grams (0.0739 mole) 1,1-dimethylhydrazine, was fitted to the flask and with the lower half of the flask at $-78^{\circ}\text{C}.$ the Wet Test Meter was set to zero.

The contents of the addition funnel was added in very small increments (one drop or less) to the frozen triethylaluminum, and the system was warmed and melted for mixing between additions. Ethane (identified by vapor phase chromatography) was the only gaseous product and the evolution was slow and controllable.

Evolution of gas was evident at temperatures as low as $-60^{\circ}\text{C}.$ for the first half of the addition, but during the second half higher temperatures (near $0^{\circ}\text{C}.$) were needed. No liquid or solid collected in the cold traps. The addition took four hours, after which the system was warmed to $25^{\circ}\text{C}.$ and stirred overnight (12 hours) to assure complete ethane evolution.

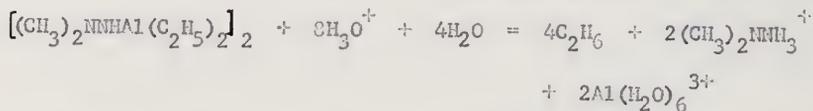
The observed, corrected volume of ethane was 1.596 liters; theory calls for 1.577 liters for the reaction



The 5 per cent excess 1,1-dimethylhydrazine was removed by pumping briefly at $45^{\circ}\text{C}./0.15$ mm. The resulting product was a colorless,

crystalline solid which weighed 10.11 grams (99.6 per cent yield, based on triethylaluminum used) and which melted at 43-44°C. (sealed tube, uncorrected).

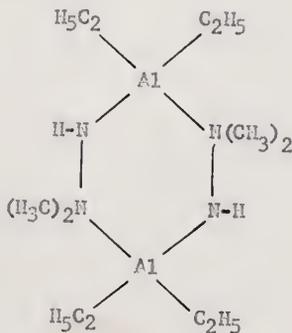
Hydrolysis of a 2.7071 gram sample of the product gave 0.845 liter of ethane. Calculated for $[(CH_3)_2NNHAl(C_2H_5)_2]_2$: 0.841 liter.



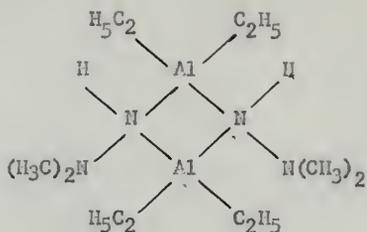
Analysis. Found: C, 50.05; H, 11.61; N, 19.70; Al, 18.57; C₂H₅, 40.78. Calcd. for $[(CH_3)_2NNHAl(C_2H_5)_2]_2$: C, 49.98; H, 11.88; N, 19.43; Al, 18.71; C₂H₅, 40.31. Molecular weight, found: 281 (cryoscopic in benzene). Calcd. for $[(CH_3)_2NNHAl(C_2H_5)_2]_2$: 288.4.

The product is soluble in most common, inert solvents. The infrared spectra obtained on a melt and 10 per cent in n-hexane show bands in the regions expected for C-H stretch and bend, N-H, N-N, C-N-N, and N-CH₃. Figures 4 and 5 show the infrared spectra.

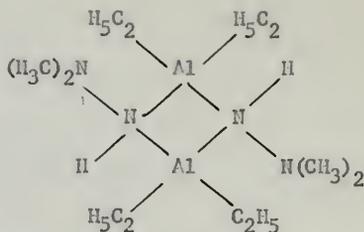
The observed molecular weight indicates a dimeric structure. Three possible structures, two of which are geometric isomers may be considered.



1. Six Membered Ring



2. Cis-Four Membered Ring



3. Trans-Four Membered Ring

The proton nuclear magnetic resonance spectrum of 2,2-dimethylhydrazinodiethylalane indicates that only one molecular species is present and shows the Al-CH₂-CH₃ and N-CH₃ structure peaks. Because of the uncertainty in position associated with the N-H group, and in addition some overlapping of peak areas, the data obtained were insufficient to use in assigning a definite structure on the basis of the spectrum alone. It is felt however, that if the structure involves the four membered ring, there might be expected two forms (cis- and trans-) in a mixture, and the n.m.r. spectrum would certainly indicate this.

Infrared data give circumstantial evidence for the six membered ring. The position of the N-H stretch in 2,2-dimethylhydrazinodiethylalane corresponds closely to that observed for tricovalent nitrogen compounds which contain the N-H group. The four membered ring does not contain this particular arrangement since it is the nitrogen atom involved in the N-H group which coordinates the aluminum atom and thus becomes tetravalent. Little importance can be placed upon these observations, however, since hydrogen bonding in the solid sample would tend to equalize the environments of the nitrogen atoms in question.

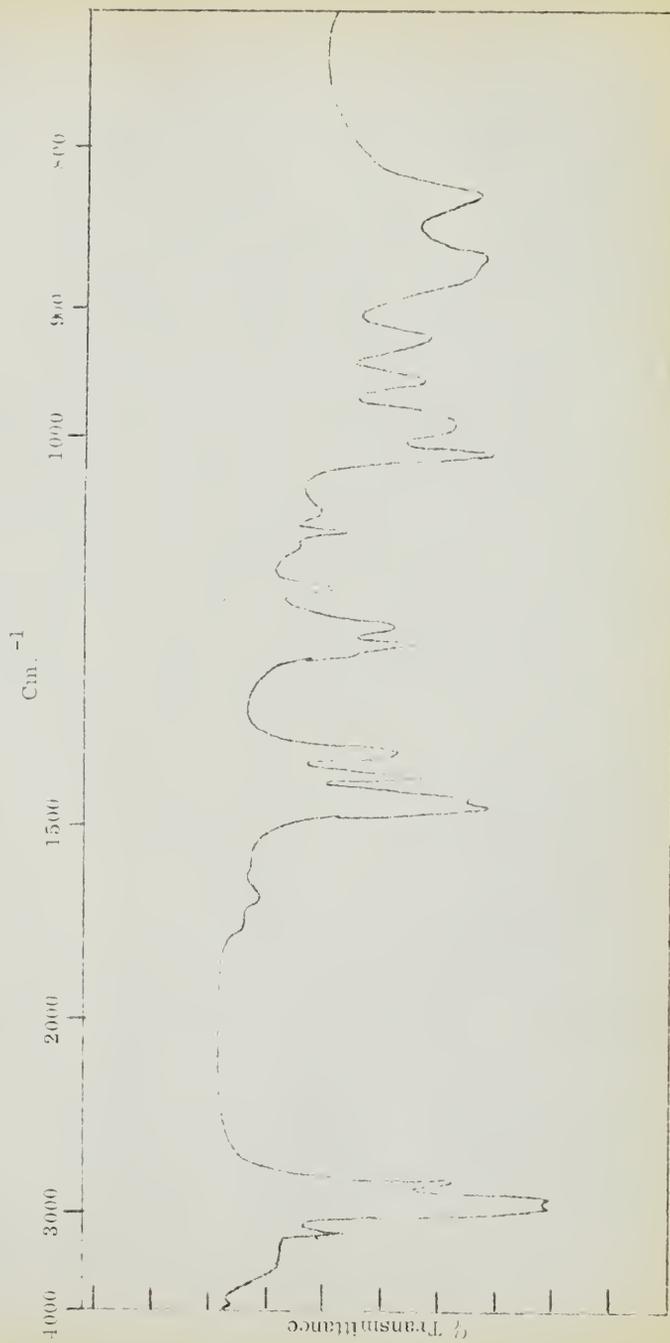


Figure 4. Infrared Spectrum of 2,2-Dimethylhydrazinodimethylalane (Melt)

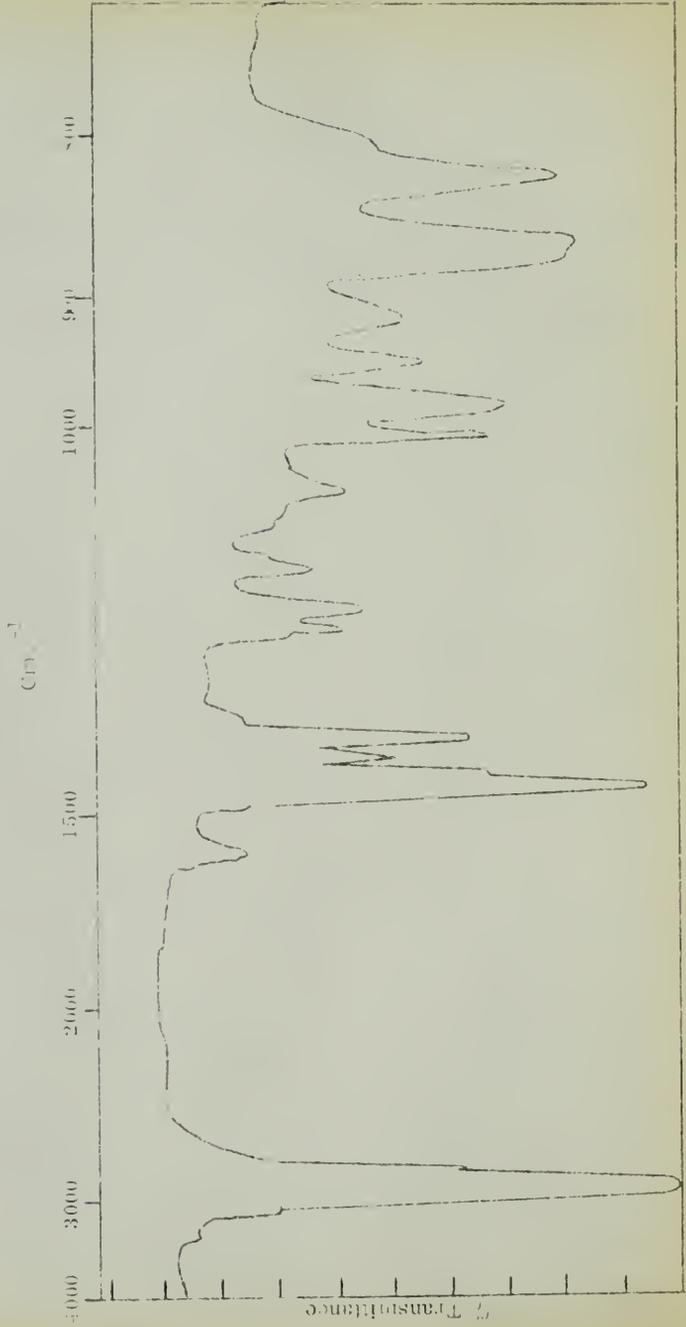


Figure 5. Infrared Spectrum of 2,2-Diethylhydrazinoethylalane (Dilute Hexane Solution)

As a possible solution to the problem of analyzing the infrared data, a sample of 2,2-dimethylhydrazinodiethylalane was run as a 10 per cent solution in *n*-hexane, where H bonding would be minimized. The resulting spectrum (Figure 5) shows little, if any, shift in the N-H stretching frequency at approximately 3150 cm.^{-1} . A new peak was observed at 1590 cm.^{-1} which is in the region usually associated with the N-H deformation frequency. This observation was not explained.

Support for the four-membered ring structure might lie in the observed peak at 1400 cm.^{-1} which is generally found in compounds containing an ammonium or substituted ammonium ion. This too, however, could be a result of hydrogen bonding in either the four or six member ring structure. The prospects for elucidating the structure of this dimer by infrared means appear rather bleak. Suggestions for further work along these lines might include a study of frequencies associated with various ring sizes which contain atoms of size similar to aluminum and nitrogen, perhaps cyclic silylhydrazines.

Pyrolytic condensation of 2,2-dimethylhydrazinodiethylalane.

In an experiment designed to test the degree of lability of the N-H bond in 2,2-dimethylhydrazinodiethylalane, a pyrolytic condensation was performed.

In the first experiment in this series the sample was heated to 195°C. at which point rapid evolution of gases caused the reaction vessel to be blown apart. The product of the reaction was a light brown solid which was very brittle and apparently highly polymeric in nature. Analysis of this solid residue for carbon, hydrogen, and nitrogen gave a ratio which corresponds to $\text{C}_{1.0} \text{H}_{3.1} \text{N}_{1.0}$ which may be

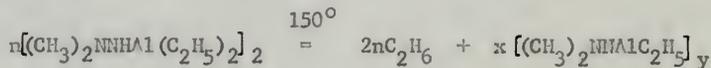
formulated as $N-N(CH_3)_2$, thus indicating that even though the material was subjected to temperatures in excess of $350^\circ C$. the dimethylhydrazino group remained intact.

This material was highly opaque to infrared and had no melting point; thus, little characterization was possible.

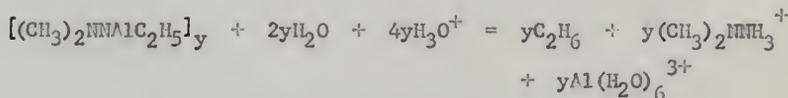
In a second experiment the condensation was run at $150^\circ C$. over a five hour period. Ethane evolution was slow and easily controlled in the temperature range $110^\circ C$. (where evolution first is observed) to $160^\circ C$. The product in this case was a dark, viscous tar which was easily soluble in benzene and hexane. The material was analyzed for active ethyl content by aqueous hydrolysis and gave the following results.

Found: C_2H_5 , 25.52. Calcd. for $[(CH_3)_2NNHAlC_2H_5]_y$, 25.46.

It thus appears that the condensation occurs according to the reaction



and the hydrolysis may be represented by the equation



Other evidence which serves to substantiate this reaction sequence is demonstrated by the conspicuous absence of the N-H absorption bands in the infrared spectrum (Figure 6). The presence of the 1,1-dimethylhydrazinium ion in the hydrolyzed sample was shown by adding aqueous sodium hydroxide until the pH was 10, and testing the vapor above the solution for a volatile free base (1,1-dimethylhydrazine) with moist red litmus, and for a reducing substance with a

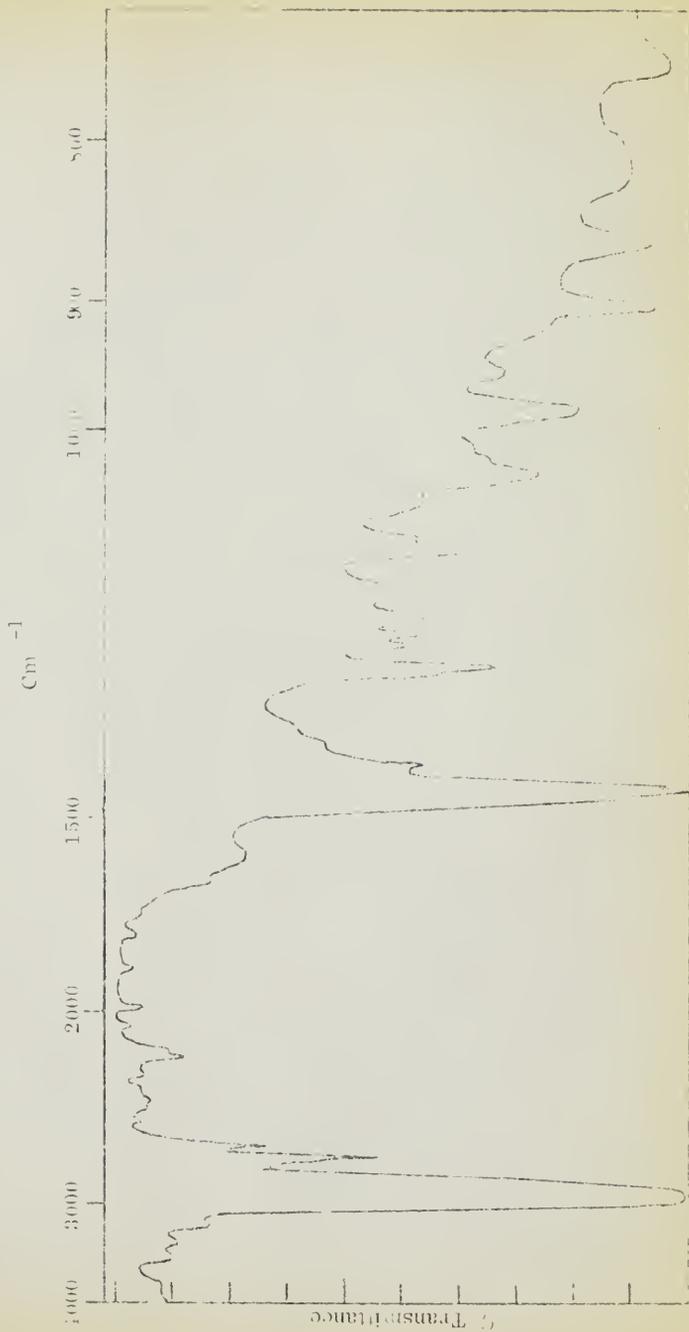


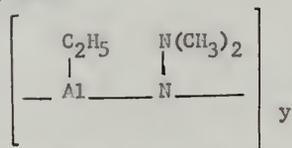
Figure 6. Infrared Spectrum of Condensation Product, $(LiAlEt_2)_3$, (Hexane Solution)

drop of KMnO_4 solution on a strip of filter paper. Both tests were positive.

A third experiment was designed to carry out the condensation as slowly as possible at a lower temperature in order to see if ethane could be removed without opening the ring or changing the degree of polymerization from a dimeric species. A sample of 2,2-dimethylhydrazinodiethylalane was heated at $75^\circ\text{C}/0.20$ mm. for a period of 144 hours. During this time the colorless, mobile liquid gradually became dark in color and grew increasingly viscous. When the reaction was complete, as evidenced by the disappearance of the N-H band in the infrared, the material had become a dark, viscous tar.

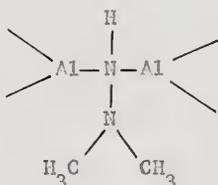
A molecular weight determination was performed cryoscopically in benzene. Molecular weight found: 646. The formula weight of a $[(\text{CH}_3)_2\text{NNAIC}_2\text{H}_5]$ unit is 114.13, thus the polymer formed in this experiment has an average degree of association, $y = 5.66$.

Possible structures for this polymer include 1) rings linked together, 2) rings larger than six member, and 3) chains with end groups of an undetermined nature. In any event, the polymer appears to have the repeating unit



The information gained in this experiment indicates that the hydrogen atom in the N-H group in 2,2-dimethylhydrazinodiethylalane is less labile than that in 1,1-dimethylhydrazine itself (or in some intermediate molecular addition complex formed prior to 2,2-dimethylhydrazinodiethylalane).

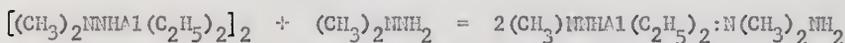
These additional data are better interpreted on the basis of a six membered ring rather than on a four membered ring. In the four membered ring the aluminum atom is coordinated by the nitrogen atom which contains the N-H group



The effect to be expected if the N-H nitrogen atom acts as a Lewis base is lebilization of the N-H bond, which is not the experimental result.

Attempted de-dimerization of 2,2-dimethylhydrazinodiethyl-
alane by adduct formation. A sample of 2,2-dimethylhydrazino-
diethylalane was mixed with a twofold excess of unsymm.-dimethyl-
hydrazine and heated to 65°C. for five hours. The product of the
reaction was a light straw liquid after the excess unsymm.-dimethyl-
hydrazine had been removed by pumping at 25°C./0.20 mm. for one hour.

The desired reaction may be represented by the following
equation:



A possible reaction that was thought unlikely would proceed via ethane
elimination



Analysis of the product of the reaction disclosed, however, that the only process that had occurred was that of partial condensation to $[(\text{CH}_3)_2\text{NNAIC}_2\text{H}_5]_y$.

Found: N, 20.05, 20.39. Calcd. for $[(\text{CH}_3)_2\text{NNAIC}_2\text{H}_5]_2$: 19.43. Calcd. for $[(\text{CH}_3)_2\text{NNAIC}_2\text{H}_5]$: 24.56. A change in the peak height of the N-H band in the infrared spectrum served to confirm the course of the reaction.

These data give an indication of the strength of the dative Al-N bond in the dimer and also seems to show that 1,1-dimethylhydrazine is capable of catalyzing the pyrolytic condensation.

Attempted de-dimerization using phosphines. Experiments in which tributylphosphine and triphenylphosphine were heated with 2,2-dimethylhydrazinodiethylalane resulted in dark, uncharacterizable, viscous liquids.

The interaction of triethylaluminum with methylhydrazine

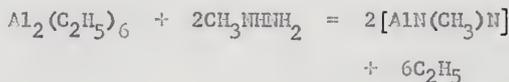
In an experiment identical in detail with that performed in the synthesis of 2,2-dimethylhydrazinodiethylalane, 1.569 grams (0.0341 mole) methylhydrazine was reacted with 3.887 grams (0.0341 mole) of triethylaluminum. Very slow dropwise addition was carried out at -78°C . with warming for melting and mixing between additions.

It was immediately apparent that the reaction was very exothermic (more so than with 1,1-dimethylhydrazine) and that a somewhat different product was being produced than was found with 1,1-dimethylhydrazine. The amount of ethane evolved approached three times the theoretical and the reaction product was a brown, inhomogeneous solid.

The total volume of ethane evolved was 2.029 liters. The amount calculated for the reaction



was 0.763 liters. For the reaction



however, the calculated volume of ethane was 2.288 liters. The quantity observed was 87.5 per cent of that required for the elimination of 3 moles of ethane per mole reaction unit.

The solid was collected and any excess triethylaluminum was removed by pumping at 25°C./0.20 mm. for five hours. An attempt to prepare a Nujol mull for infrared analysis resulted in spontaneous combustion of the solid upon contact with air. Whether this was due to the material itself or unremoved triethylaluminum is not known.

The infrared spectrum was obtained on a mull prepared in the dry box and was very opaque, which is characteristic of highly polymeric materials. A very weak N-H peak showed that the reaction had not gone to completion.

Analysis. Found: Al, 37.15 per cent. Calcd. for $\text{CH}_3\text{N}_2\text{Al}$: Al, 38.55 per cent.

The material was found to be insoluble in all the solvents tried, and dissolved only with very great reluctance in hot 15M nitric acid. The nitric acid solution was highly colored, but was decolorized with hydrogen peroxide in order for aluminum analysis to be run on the solution.

The solid has no melting point, but chars when heated to 360°C.

Discussion

Although there were not a large amount of data collected in our study of the interactions of 1,1-dimethylhydrazine and methylhydrazine with triethylaluminum, certain interesting differences were noted in the behavior of the two different hydrazines and in the behavior of hydrazines and amines with respect to their interactions with aluminum alkyls. One pleasing result of this work is the synthesis and characterization of the new compound, 2,2-dimethylhydrazinodiethylalane. Although a recent publication (21) reports methylaluminum derivative of hydrazines, this compound is the sole known ethylaluminum derivative of a hydrazine.

An idea which was a motivating factor in the initial phases of this work concerned the possibility of preparing a solid adduct between triethylaluminum and 1,1-dimethylhydrazine. Both the alane and the hydrazine are mobile liquids and both have been used as liquid propellants in the missile industry and in the U. S. space effort. For many reasons solid fuels are preferred to liquids in certain types of applications. Thus, a solid adduct formed from the two liquids might well be an interesting fuel.

From the preceding description of the observations made of the interaction of triethylaluminum with 1,1-dimethylhydrazine it can be seen that no adduct was found in the temperature range studied. It is possible, of course, that work at very low temperatures would

produce evidence indicating the formation of such an adduct, but in any case no such compound exists above -60°C . Similar results were encountered in the reaction of triethylaluminum with monomethylhydrazine.

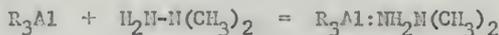
Of the various nitrogen donor-alane systems which are known, those systems containing a hydrazine are certainly the most reactive. Of the reported amine-alanes, where the amine may or may not contain the NH_2 group, it may be generally said that the adduct formed between the amine and the alane is stable at room temperature. In the case of hydrazine-alanes, however, none have been reported which contain the NH_2 group except $(\text{CH}_3)_2\text{N}(\text{NH})\text{Al}(\text{CH}_3)_2:\text{NH}_2\text{N}(\text{CH}_3)_2$ which is not a simple hydrazine-alane. (21)

An approach to a clearer understanding of the nature of the hydrazine-alanes, the hydrazinoalanes, and their condensation products may lie in a stepwise consideration of the interactions involved in the formation of these compounds.

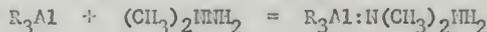
Any acceptable mechanism must be consistent with the following known facts: 1) the reaction was carried out in such a way as to have an excess of triethylaluminum present in the reaction mixture until addition of 1,1-dimethylhydrazine was essentially complete, 2) ethane evolution occurred at -60°C . during the first half of the reaction, but was less rapid during the second half and required higher temperatures, $0-10^{\circ}\text{C}$., 3) the product is a dimer, and 4) the N-H group in the product is less active than that in 1,1-dimethylhydrazine.

Fetter and Bartocha (21) have recently made statements concerning proposed mechanisms of interaction and the structure of hydrazinoalanes. They believe that a plausible first step in the interaction

of 1,1-dimethylhydrazine with an aluminum alkyl is the coordination of the $-NH_2$ end of the molecule with the AlR_3 unit,

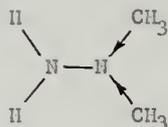


rather than coordination of the $-N(CH_3)_2$ end, as shown below:



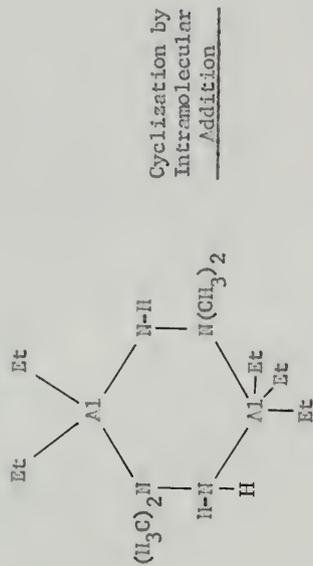
The reason for their choice is the fact that their preparations of dimethylhydrazinoalanes produce as a gaseous product, $R-H$, rather than $R-CH_3$. From a consideration of the bond energies alone, $N-H$ (92 kcal./mole), and $N-C$ (66 kcal./mole), one might favor such an interpretation. However, if there are kinetic effects which favor a different reaction, there is no reason to dismiss coordination by the $-N(CH_3)_2$ end of 1,1-dimethylhydrazine.

If we first accept the premise that the $-N(CH_3)_2$ end of the $H_2NN(CH_3)_2$ molecule is more basic than the $-NH_2$ end because of the inductive effect of the methyl groups,

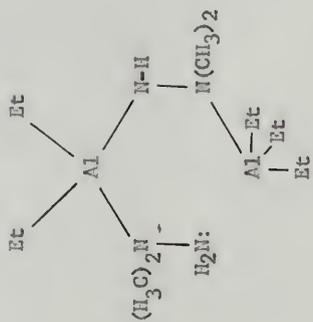


then in the presence of the strong Lewis acid, $AlEt_3$, we should expect the initial coordination as shown in equation 1 on page 30.

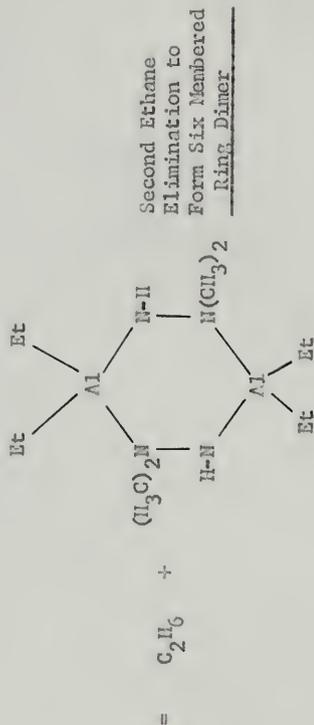
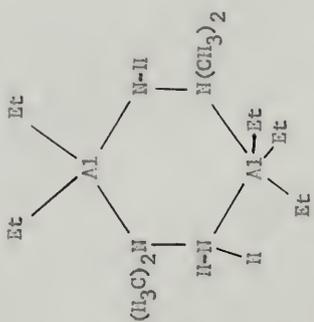
In the presence of a large excess of Lewis acid, $AlEt_3$, we would expect a second step (equation 2) to occur very quickly, to form the bis- complex, $Et_3Al:NH_2-N(CH_3)_2:AlEt_3$.



=



5.

= C₂H₆ +

6.

The decomposition of the bis- complex to ethane and the AlEt_3 adduct of the hydrazinoalane, $\text{Et}_2\text{AlNHN}(\text{CH}_3)_2:\text{AlEt}_3$, would follow according to equation 3. At this point the stoichiometry is a 2:1 ratio of alane to hydrazine, and it is at this point in the preparation where the temperature at which ethane will evolve suddenly changes to a higher value. In fact it has been observed in the laboratory that the remaining addition of 1,1-dimethylhydrazine may be made quickly at -25°C . and that no appreciable gas evolves until the mixture is warmed to 0°C .

In the presence of additional free 1,1-dimethylhydrazine addition would be expected according to equation 4, followed by cyclization as shown in equation 5, and ethane elimination to the final cyclic six membered ring dimer as in equation 6.

A suggestion for further work in this system appears quite obvious at this point. If the mechanism proposed above is correct there should exist the possibility of preparing $\text{Et}_2\text{Al-NHN}(\text{CH}_3)_2:\text{AlEt}_3$ by the reaction of the alane with the hydrazine in a 2:1 mole ratio. The prospects for preparing any of the other intermediates do not appear promising, however. It is quite possible that $\text{Et}_2\text{Al-NHN}(\text{CH}_3)_2:\text{AlEt}_3$ would not be isolated as a monomer since it could very well associate to form dimers or chain polymers; these species would probably react in much the same manner as the monomer with 1,1-dimethylhydrazine, although less vigorously. An interesting point is that if this material did exist as a monomer, it would indicate that the need of aluminum for an electron pair was being satisfied by the adjacent nitrogen atom which has an unshared pair of electrons available.

This observation would provide evidence for the existence of pi-bonding between aluminum and nitrogen, which has been discounted by Laubengayer (30).

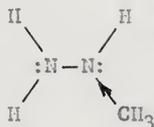
Condensation of 2,2-dimethylhydrazinodiethylalane. Since it has not been observed that ethane is intramolecularly eliminated, a process which would result in the formation of $[(CH_3)_2NHAIC_2H_5]_2$, with a molecular weight of about 228, it appears reasonable to assume that the mechanism of the condensation involves attack of an N-H group on the $Al(C_2H_5)_2$ group in 2,2-dimethylhydrazinodiethylalane. This condition could only be fulfilled if the N-H group has an unshared pair of electrons and can act as a Lewis base; thus it does not appear that the four membered ring structure, page 17, can participate in such a condensation reaction.

In the presence of excess 1,1-dimethylhydrazine it was found that the condensation proceeds at a lower temperature than is observed when pure 2,2-dimethylhydrazinodiethylalane is condensed by heating. Thus it appears that the presence of N-H groups (with free electron pairs) is necessary for the condensation reaction.

These observations leave doubt that a dimeric condensation product will be observed since intramolecular elimination of ethane in the ring apparently does not occur, as evidenced by the observed high molecular weight of the condensation product.

Condensation of triethylaluminum with methylhydrazine. The observations made on this system tend to corroborate the mechanism suggested for the interaction of triethylaluminum with 1,1-dimethylhydrazine.

In methylhydrazine we should expect, from considerations of the inductive effect, that the most acidic N-H bond is on the -NH_2 end of the molecule and that the stronger Lewis base is the $\text{-N(CH}_3\text{)H}$ end.



Once a methylhydrazine molecule donates an electron pair, however, there is some question as to which N-H bond is most acidic.

An initial attack of methylhydrazine on triethylaluminum would produce the molecular complex $\text{Et}_3\text{Al:NHCH}_3\text{NH}_2$, which could either eliminate ethane intra- or intermolecularly. The inhomogeneity of the product may serve to indicate that both these processes occur, or that at any rate, molecular species are produced in various degrees of association.

Considering the abundance of active N-H groups in the initial adduct, it is not surprising that complete condensation to $[\text{AlN(CH}_3\text{)N}]_y$ is the final product.

Although it is not implicit in the formulation of this polymeric species, it is expected that aluminum achieves a covalency of four, either by accepting a pair of electrons from a nearby nitrogen atom or by accepting a pair of electrons from an adjacent nitrogen atom. The fact that the polymer appears to be a highly extended network would lend support to the former suggestion.

Conclusion

The results of our study of the interactions of triethylaluminum with two different alkyl hydrazines has resulted in the synthesis of three new species, $[(CH_3)_2NNHAl(C_2H_5)_2]_2$, $[(CH_3)_2NNHAlC_2H_5]_x$, $[AlN(CH_3)N]_y$, and has given various data through observation of reactivities, stoichiometries, and reaction conditions. Some physical characterization was possible, and all available tools were employed in an attempt to elucidate the structure of 2,2-dimethylhydrazinodiethylalane, which is thought to have a six membered ring structure.

A mechanism for the formation of these species consistent with the observed data is suggested and applied to both this work and some additional work reported in the literature.

Although no evidence for pi-bonding between aluminum and nitrogen has been found, it is certainly within the realm of possibility that such bonding may exist. Preparation of the intermediate, $Et_2AlNHN(CH_3)_2:AlEt_3$, in a monomeric form would lend more credence to the possibility of aluminum forming pi-bonds with nitrogen.

Further study is indicated.

CHAPTER II

REACTIONS OF ARYLHALOPHOSPHINES AND DERIVATIVES OF ARYLHALOPHOSPHINES WITH SEVERAL ALKYL HYDRAZINES

Introduction

The field of phosphorus-nitrogen chemistry has been periodically reviewed and there are two major reference texts (32,33) and an excellent review article (34) which although not chiefly devoted to phosphorus-nitrogen chemistry certainly provide a foundation for the worker in this field. No up-to-date listing of phosphorus-nitrogen compounds is available, however. Particularly lacking are reference summaries in the area of the hydrazine derivatives of phosphines and phosphorus acids.

A thorough compilation of all known hydrazine derivatives of the phosphines and related compounds was prepared in order to determine the extent to which these materials have been studied and to what use the information has been put. As a result of this survey it has been found that hydrazinophosphine, H_2PNH_2 , has never been reported, nor have any of its organic derivatives. Most of the work with hydrazinophosphorus compounds has been in the area of hydrazine derivatives of the esters of phosphorus acids.

There exist, on the basis of the more common substituents for phosphorus, a great variety of possible classes of compounds containing the hydrazinophosphorus group, -P-N-N-, but the survey shows that work

has been done on only a few of the possible series of such compounds. Many of the compounds reported in this dissertation are the only known members of their series of compounds.

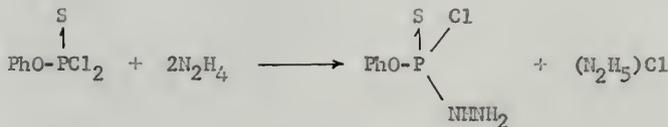
The general method of preparation of hydrazine derivatives of organophosphorus compounds is analogous to the methods used for the syntheses of aminophosphines and aminophosphorus compounds (35,36). The hydrazine is usually dissolved in an anhydrous solvent and the resulting solution is added to a halophosphorus compound dissolved in the same solvent. Excess hydrazine can be used to absorb the hydrogen halide produced in the reaction, or a tertiary amine such as triethylamine or pyridine may be used for this purpose.

Example (37):



The monohydrazinophosphorus compounds which have been reported in the literature are listed in Tables 11-14 along with pertinent data; bis- and tris-hydrazinophosphorus compounds comprise Tables 15-17.

Recent work has shown that stepwise substitution of chlorine can be obtained in some arylphosphorodichloridothioates by partial solvolysis (38):

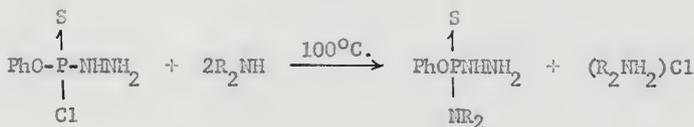


The remaining chlorine is found to be less labile as a result of the substitution of the less electronegative hydrazino group and is

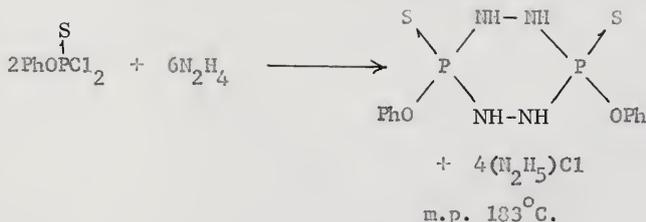
thus resistant to further solvolysis. In some cases the compounds can be water-washed without appreciable hydrolysis. Arylphosphorochloridohydrazidothioates are listed in Table 13.

The second chlorine in these molecules can be made to undergo solvolysis at higher temperatures, and in the presence of water, form arylphosphorohydrazidothioic acids, while in the presence of amines the various arylphosphoroamidohydrazidothioates are formed (see Tables 19 and 20).

Example:



An effect of changing the reactant ratio has been observed in the formation (in small yield) of a cyclic compound (39):



A scheme devised by A. Michaelis is responsible for the synthesis of amino-bis(hydrazino)phosphine oxides (40). He found that amidophosphonic dichlorides can be prepared by refluxing a mixture of phosphoryl chloride and a secondary amine hydrochloride until HCl evolution ceases:

TABLE 11
Alkyl and Aryl Phosphorohydrazidates

Product	Yield	m.p.	Reference
$(C_2H_5O)_2\overset{O}{P}NHNHPh$	n.a.	113-114°	41
$(PhO)_2\overset{O}{P}NHNH_2$	n.a.	112°	42
$(PhCH_2O)_2\overset{O}{P}NHNH_2$	95%	73°	43
$(CH_2=CHCH_2O)_2\overset{O}{P}NHNHPh$	76%	85-87°	42
$(CH_3O)_2\overset{O}{P}NHNHPh$	93%	132-134°	42
$CH_3O(C_2H_5O)\overset{O}{P}NHNHPh$	82%	77.5-80.5°	42

n.a. - not available.

TABLE 12

Alkyl and Aryl Phosphorohydrazidothioates

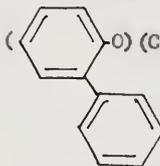
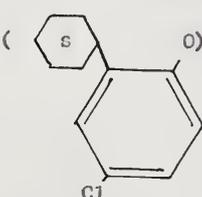
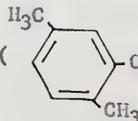
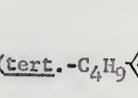
Product	Yield	m.p./b.p.	Reference
$(\text{PhO})_2 \overset{\text{S}}{\text{P}}\text{NHNH}_2$	---	m. 63°	39, 44
$(\text{PhO})(\text{CH}_3\text{O}) \overset{\text{S}}{\text{P}}\text{NHNH}_2$	73%	no distillate at 0.01 mm. Hg	45
$(\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{O})(\text{CH}_3\text{O}) \overset{\text{S}}{\text{P}}\text{NHNH}_2$	68%	m. 103°	45, 46
$(\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{O})(\text{CH}_3\text{O}) \overset{\text{S}}{\text{P}}\text{NHNH}_2$	---	--	46
$(\text{C}_6\text{H}_5-\text{O})(\text{CH}_3\text{O}) \overset{\text{S}}{\text{P}}\text{NHNH}_2$ 	---	m. 76-77°	46
$(\text{C}_6\text{H}_4(\text{S})-\text{O})(\text{CH}_3\text{O}) \overset{\text{S}}{\text{P}}\text{NHNH}_2$ 	---	m. 85-87°	46
$(\text{H}_3\text{C}-\text{C}_6\text{H}_3(\text{CH}_3)-\text{O})(\text{CH}_3\text{O}) \overset{\text{S}}{\text{P}}\text{NHNH}_2$ 	---	--	46
$(\text{tert.}-\text{C}_4\text{H}_9-\text{C}_6\text{H}_3(\text{Br})-\text{O})(\text{CH}_3\text{O}) \overset{\text{S}}{\text{P}}\text{NHNH}_2$ 	---	m. 92.5-93.5°	46

TABLE 12 Continued

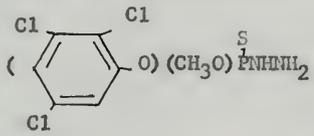
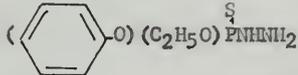
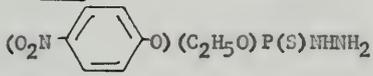
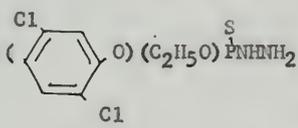
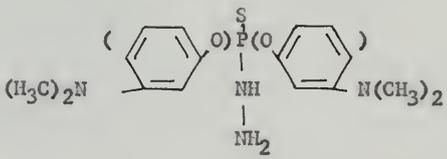
Product	Yield	m.p./b.p.	Reference
 $(\text{C}_6\text{Cl}_4\text{O})(\text{CH}_3\text{O})\text{P}(\text{S})\text{NHNH}_2$	---	m. 88-88.5°	46
 $(\text{C}_6\text{H}_5\text{O})(\text{C}_2\text{H}_5\text{O})\text{P}(\text{S})\text{NHNH}_2$	85%	b. 147-150°	45
 $(\text{O}_2\text{N-C}_6\text{H}_4\text{O})(\text{C}_2\text{H}_5\text{O})\text{P}(\text{S})\text{NHNH}_2$	63%	m. 80°	45
 $(\text{C}_6\text{H}_3\text{Cl}_2\text{O})(\text{C}_2\text{H}_5\text{O})\text{P}(\text{S})\text{NHNH}_2$	91%	no distillate at 0.01 mm. Hg	45
 $(\text{H}_3\text{C})_2\text{N-C}_6\text{H}_4\text{O-P}(\text{S})(\text{NH}_2)\text{O-C}_6\text{H}_4\text{N}(\text{CH}_3)_2$	---	m. 117-118°	47

TABLE 13

Alkyl and Aryl Phosphorophenylhydrazidothioates

Product	Yield	m.p.	Reference
$(C_2H_5O)_2 \overset{S}{P}NHNHPh$	---	68-69°	41
$(PhO)(CH_3O) \overset{S}{P}NHNHPh$	42%	80°	45
$(PhO)(C_2H_5O) \overset{S}{P}NHNHPh$	35%	57°	45
$(O_2N-C_6H_4-O)(CH_3O) \overset{S}{P}NHNHPh$	73%	125-127°	45
$(O_2N-C_6H_4-O)(C_2H_5O) \overset{S}{P}NHNHPh$	65%	68°	45
$(Cl-C_6H_3-O)(C_2H_5O) \overset{S}{P}NHNHPh$	59%	108-110°	45
$(Cl-C_6H_3-O)(C_2H_5O) \overset{S}{P}NHNHPh$	81%	62°	45
$(N(CH_3)_2-C_6H_4-O)_2 \overset{S}{P}(O-C_6H_4-N(CH_3)_2)NHNH-C_6H_5$	---	146-147.5°	47

TABLE 14
Phenylhydrazidoalkylphosphonates

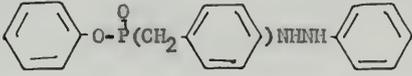
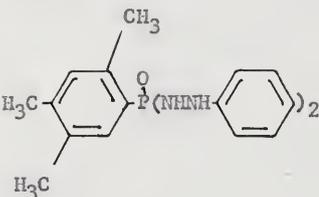
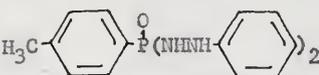
Product	Yield	m.p.	Reference
$\text{C}_2\text{H}_5\text{O}-\overset{\text{O}}{\parallel}{\text{P}}(\text{CCl}_3)\text{NHNHPh}$	---	154-156.5°	42
	---	173-174°	48, 49

TABLE 15

Bis(hydrazino)phenylphosphine Oxides

Product	Yield	m.p.	Reference
$\text{PhP}(\text{NHNH}_2)_2$	---	131°	50
$\text{PhP}(\text{NHNHPh})_2$	---	175°	48
	---	208°	51
	---	171°	49

A Bis(hydrazino)phenylphosphine Sulfide

Product	Yield	m.p.	Reference
$\text{PhP}(\text{NHNH}_2)_2$	---	115°	50

TABLE 16

Arylphosphorodihydrazidothioates

Product	Yield	m.p.	Reference
$\text{PhO}-\overset{\text{S}}{\underset{ }{\text{P}}}(\text{NHNH}_2)_2$	24%	95° (103°)	43, 52
$\text{PhO}-\overset{\text{S}}{\underset{ }{\text{P}}}(\text{NHNHPh})_2$	---	136°	53
$\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{O}-\overset{\text{S}}{\underset{ }{\text{P}}}(\text{NHNH}_2)_2$	---	106°	52
$\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{O}-\overset{\text{S}}{\underset{ }{\text{P}}}(\text{NHNH}_2)_2$	90%	142°	45
$\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{O}-\overset{\text{S}}{\underset{ }{\text{P}}}(\text{NHNHPh})_2$	87%	176°	45
$\text{Cl}-\text{C}_6\text{H}_4-\text{O}-\overset{\text{S}}{\underset{ }{\text{P}}}(\text{NHNH}_2)_2$	93.7%	145-147°	38
$\text{Cl}_3-\text{C}_6\text{H}_2-\text{O}-\overset{\text{S}}{\underset{ }{\text{P}}}(\text{NHNH}_2)_2$	93.5%	152-153°	38, 54
$\text{Cl}-\text{C}_6\text{H}_3(\text{Cl})_2-\text{O}-\overset{\text{S}}{\underset{ }{\text{P}}}(\text{NHNHPh})_2$	96.7%	156-157°	38, 54
$\text{Cl}_3-\text{C}_6\text{H}_2-\text{O}-\overset{\text{S}}{\underset{ }{\text{P}}}(\text{NHNHPh})_2$	73%	158-159°	38

TABLE 16 Continued

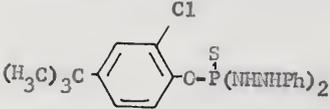
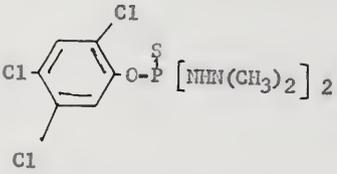
Product	Yield	m.p.	Reference
	92.3%	151-153°	38
	93.5%	123-125°	38, 54

TABLE 17

Tris(hydrazino)phosphine Oxides and Sulfides

Product	Yield	m.p.	Reference
<u>OXIDES</u>			
$\begin{array}{c} \text{O} \\ \\ \text{P}(\text{NHNH}_2)_3 \end{array}$	75%	--	43
$\begin{array}{c} \text{O} \\ \\ \text{P}(\text{NHNHPh})_3 \end{array}$	---	196°	55
$\begin{array}{c} \text{O} \\ \\ \text{P}(\text{NHNH} \text{---} \text{C}_6\text{H}_4 \text{---} \text{CH}_3)_3 \end{array}$	---	189°	55
<u>SULFIDES</u>			
$\begin{array}{c} \text{S} \\ \\ \text{P}(\text{NHNH}_2)_3 \end{array}$	---	unstable	44
$\begin{array}{c} \text{S} \\ \\ \text{P}(\text{NHNHPh})_3 \end{array}$	---	154°	55
$\begin{array}{c} \text{S} \\ \\ \text{P}(\text{NHNH} \text{---} \text{C}_6\text{H}_4 \text{---} \text{CH}_3)_3 \end{array}$	---	unstable	55

TABLE 18
Arylphosphorochloridohydrazidothioates

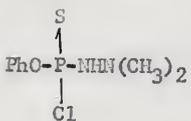
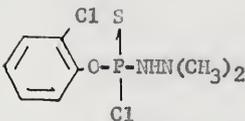
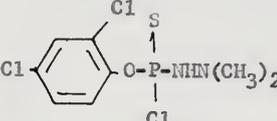
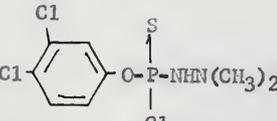
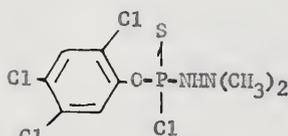
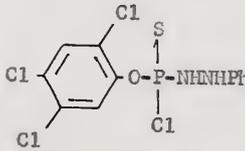
Product	Yield	m.p.	Reference
	97.1%	--	38
	95.8%	--	38
	99.0%	74-75°	38
	84%	--	38
	100%	76-78°	38
	79%	120-122°	38

TABLE 19

Alkylphosphorohydrazidoic Acids*

Product	Yield	m.p.	Reference
$\begin{array}{c} \text{O} \\ \uparrow \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{NHNH}-\text{C}_6\text{H}_4-\text{CH}_3 \\ \\ \text{OH} \end{array}$	--	195° (d.)	52
$\begin{array}{c} \text{O} \\ \uparrow \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{NHNH}-\text{C}_6\text{H}_4-\text{Br} \\ \\ \text{OH} \end{array}$	--	187°	52
$\begin{array}{c} \text{O} \\ \uparrow \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{NHNHPh} \\ \\ \text{OH} \end{array}$	--	192° (d.)	52
$\begin{array}{c} \text{O} \\ \uparrow \\ \text{C}_2\text{H}_5\text{O}-\text{P}-\text{NHNH}_2 \\ \\ \text{OH} \end{array}$	--	100°	52

*See TABLE 3 for examples of salts of acids of this type.

TABLE 20

Arylphosphoroamidohydrazidothioates

Product	Yield	m.p.	Reference
	75%	86-87°	38
	87%	137-139°	38
	90.5%	104-105°	38
	100%	131-132°	38
	44%	112-113°	38



The amino-bis(hydrazino)phosphine oxide is the product obtained upon hydrazinolysis of the amidophosphonic dichloride:

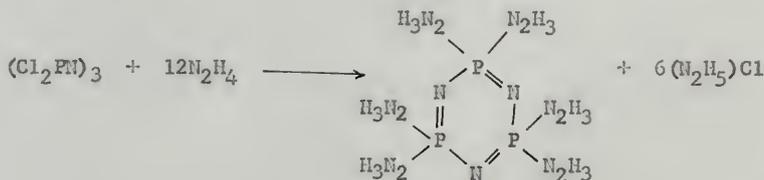


Tables 21 and 22 list the reported amino-bis(hydrazino)-phosphine oxides and sulfides.

An example of another reaction which produces mixed amino-hydrazino derivatives of arylphosphonic acid involves a transamination reaction (56):



Hydrazinolysis of the phosphonitrilic chloride trimer is also known (57, 58):



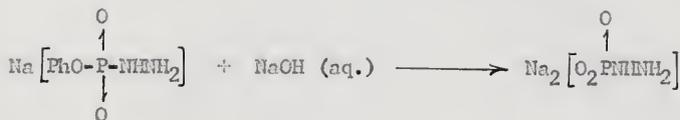
Reactions

The reactions of the hydrazine derivatives of organo-phosphorus compounds are interesting in that they may help to determine the structure of the compounds and in many cases lead to entirely new classes of compounds. The reactions are frequently troublesome and may occur as side reactions during the preparation of the desired compound and thus lower the yield.

The P-N bond is susceptible to hydrolysis and the degree to which this occurs depends in large part on the nature of the substituents on the phosphorus atom and whether or not the phosphorus is in either of the oxidized states, the oxide or the sulfide. In some cases, especially when the compound contains an ester group, it is not the P-N bond which undergoes hydrolysis initially, but the ester group (37, 43):



Further hydrolysis will yield a salt of the phosphorus acid



and the free acid can be obtained by metathesis:



Complete hydrolysis is obtained by prolonged boiling in aqueous sodium hydroxide and yields free hydrazine and the phosphate ion:



Table 23 lists some hydrolysis products obtained in this manner.

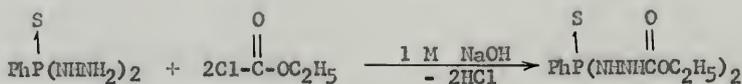
Hydrolysis does not always occur in the manner described above, but may immediately attack the P-N bond as in the illustration below (50):



In this case hydrolysis occurs so readily as to preclude the existence of the hydrazine derivative in the presence of water.

The former behavior is typical of esters of phosphoric acid and the latter is generally observed for derivatives of phosphonic acid.

Hydrolysis is a competing reaction when a hydrazine derivative of an organophosphorus compound is treated with a chloroester, consequently low yields are to be expected for a reaction of this nature (50):



m.p. 133°C. (46 per cent)

TABLE 21

Amino-bis(hydrazino)phosphine Oxides

Product	Yield	m.p.	Reference
<u>Primary</u>			
$\text{C}_2\text{H}_5\text{NH}-\overset{\text{O}}{\underset{\text{ }}{\text{P}}}(\text{NHNHPh})_2$	--	153°	40
$\text{n-C}_3\text{H}_7\text{NH}-\overset{\text{O}}{\underset{\text{ }}{\text{P}}}(\text{NHNHPh})_2$	--	151°	40
$\text{iso-C}_4\text{H}_9\text{NH}-\overset{\text{O}}{\underset{\text{ }}{\text{P}}}(\text{NHNHPh})_2$	--	141°	40
$\text{n-C}_5\text{H}_{11}\text{NH}-\overset{\text{O}}{\underset{\text{ }}{\text{P}}}(\text{NHNHPh})_2$	--	122°	40
<u>Secondary</u>			
$(\text{CH}_3)_2\text{N}-\overset{\text{O}}{\underset{\text{ }}{\text{P}}}(\text{NHNHPh})_2$	--	194-195°	40
$(\text{C}_2\text{H}_5)_2\text{N}-\overset{\text{O}}{\underset{\text{ }}{\text{P}}}(\text{NHNHPh})_2$	--	184-185°	40
$(\text{n-C}_3\text{H}_7)_2\text{N}-\overset{\text{O}}{\underset{\text{ }}{\text{P}}}(\text{NHNHPh})_2$	--	164°	40
$(\text{iso-C}_4\text{H}_9)_2\text{N}-\overset{\text{O}}{\underset{\text{ }}{\text{P}}}(\text{NHNHPh})_2$	--	168°	40
$\text{PhN}(\text{CH}_3)-\overset{\text{O}}{\underset{\text{ }}{\text{P}}}(\text{NHNHPh})_2$	--	148°	40

TABLE 22

Amino-bis(hydrazino)phosphine Sulfides

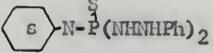
Product	Yield	m.p.	Reference
<u>Primary</u>			
$\text{iso-C}_4\text{H}_9\text{NH}-\overset{\text{S}}{\underset{\text{S}}{\text{P}}}(\text{NHNHPh})_2$	--	129°	40
<u>Secondary</u>			
$(\text{C}_2\text{H}_5)_2\text{N}-\overset{\text{S}}{\underset{\text{S}}{\text{P}}}(\text{NHNHPh})_2$	--	--	40
$(\text{n-C}_3\text{H}_7)_2\text{N}-\overset{\text{S}}{\underset{\text{S}}{\text{P}}}(\text{NHNHPh})_2$	--	196°	40
 $\text{N}-\overset{\text{S}}{\underset{\text{S}}{\text{P}}}(\text{NHNHPh})_2$	--	158°	40

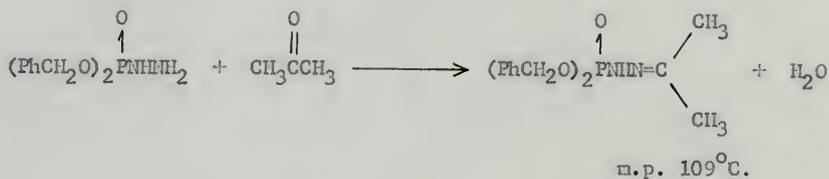
TABLE 23

Salts of Phosphorohydrazidates

Product	m.p.	Reference
Na (PhOPO ₂ NHNH ₂)	--	37, 43
Na ₂ (OPO ₂ NHNH ₂)	--	37
Na ₂ (OPO ₂ NHNH ₂) · H ₂ O	--	43
Na (HOPO ₂ NHNH ₂)	--	37
K (PhOPO ₂ NHNH ₂)	--	43
K (HOPO ₂ NHNH ₂)	--	37
NH ₄ (PhOPO ₂ NHNH ₂)	--	37
Ba (PhOPO ₂ NHNH ₂) ₂	--	37
Ba (OPO ₂ NHNH ₂)	--	37
Pb (PhOPO ₂ NHNH ₂) ₂	--	37
Pb (OPO ₂ NHNH ₂)	--	37

$\begin{array}{c} \text{O} \\ \\ \text{PhCH}_2\text{OPNHNH}_2 \\ \\ \text{OH} \end{array}$	--	43
Na (PhCH ₂ OPO ₂ NHNH ₂)	--	43
K (PhCH ₂ OPO ₂ NHNH ₂)	--	43

Hydrazone formation has been observed in compounds where the water produced in the reaction does not appreciably hydrolyze the reactants or products (43):



Other such known hydrazones are listed in Tables 24 and 25. Both aldehydes and ketones have been used to prepare such hydrazones and the reaction is apparently general for hydrazine derivatives which contain the $-\text{NH}_2$ group.

When an arylphosphorohydrazidate is treated with anhydrous hydrogen chloride salt formation is observed (43):



This reaction is analogous to the formation of hydrazinium salts and the proton attack invariably occurs on the most nucleophilic nitrogen atom (59).

Quarternization reactions using methyl iodide have been reported, but the reactions described are not always similar to the reaction described above with hydrogen chloride. Instead, it is found that some nucleophilic centers will quarternize in preference to the nitrogen atoms contained in the hydrazino group (47).

TABLE 24

Benzylidene Derivatives of Alkylphosphorohydrazidates

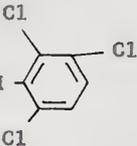
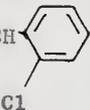
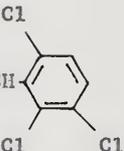
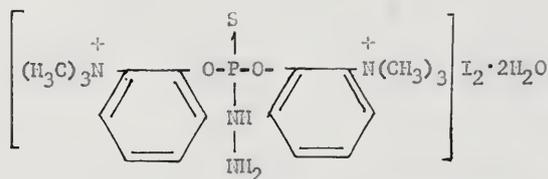
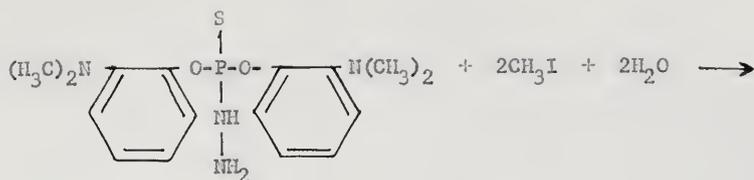
Product	m.p.	Reference
$(\text{CH}_3\text{O})_2\overset{\text{O}}{\text{P}}\text{N}(\text{CH}_3)\text{N}=\text{CH}$ 	69-71°	60
$(\text{CH}_3\text{O})_2\overset{\text{O}}{\text{P}}\text{NHN}=\text{CH}$ 	123-124°	60
$(\text{C}_2\text{H}_5\text{O})_2\overset{\text{O}}{\text{P}}\text{NHN}=\text{CH}$ 	52-53°	60
$(\text{C}_2\text{H}_5\text{O})_2\overset{\text{O}}{\text{P}}\text{N}(\text{CH}_3)\text{N}=\text{CH}$ 	54-55°	60
$(\text{C}_2\text{H}_5\text{O})_2\overset{\text{O}}{\text{P}}\text{NHN}=\text{CH}$ 	122-123°	60

TABLE 25

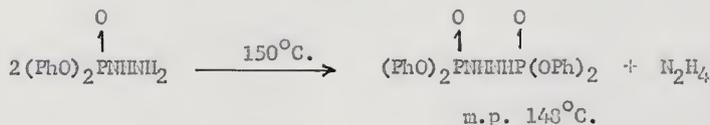
Hydrazones of Bis(hydrazino)phenylphosphine Oxides-
 Hydrazones of Bis(hydrazino)phenylphosphine Sulfides

Product	m.p.	References
$\text{Ph}-\overset{\text{O}}{\underset{ }{\text{P}}}(\text{NHN}=\text{C}(\text{CH}_3)_2)_2$	170°	58
$\text{Ph}-\overset{\text{O}}{\underset{ }{\text{P}}}(\text{NHN}=\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4\text{Cl})_2$	201°	58
$\text{Ph}-\overset{\text{O}}{\underset{ }{\text{P}}}(\text{NHN}=\text{CH}-\text{C}_6\text{H}_4\text{CH}_3)_2$	171°	58
$\text{Ph}-\overset{\text{S}}{\underset{ }{\text{P}}}(\text{NHN}=\text{C}(\text{CH}_3)_2)_2$	155°	58
$\text{Ph}-\overset{\text{S}}{\underset{ }{\text{P}}}(\text{NHN}=\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4\text{Cl})_2$	162°	58
$\text{Ph}-\overset{\text{S}}{\underset{ }{\text{P}}}(\text{NHN}=\text{C}(\text{CH}_2)_4\text{CH}_2)_2$	133°	58



m.p. 156-158°C. (dec.)

The final reaction to be mentioned here is that of condensation. This type of reaction is potentially very promising as a preparative method and occurs with the intermolecular elimination of hydrazine at elevated temperatures (37):



The product of this reaction was synthesized by another route in order to confirm its identity (43).

With respect to the practical applications of hydrazino-phosphorus compounds, several patents have been granted which relate to the use of these materials as insecticides, fungicides, nematocides, and fertilizers.

Experimental and Results

Materials

Hydrazines. 1,1-Dimethylhydrazine and methylhydrazine are both commercially available. The samples used in this work were purified prior to use by distillation from calcium hydride. The reagents thus purified possessed very narrow boiling ranges: 1,1-dimethylhydrazine, 62.2-63.0°C./758 mm., methylhydrazine, 87.3-88.0°C./761 mm. All hydrazines were stored in air-tight glass containers in a cool, dark location.

1,1,2-Trimethylhydrazine was prepared from 1,1-dimethylhydrazine by the method of Class, et al. (61); similarly, 1-ethyl-2,2-dimethylhydrazine was prepared as reported by Klages, et al. (62). Both were distilled from calcium hydride or lithium aluminum hydride and boiled in the ranges 58-62°C. and 92-93°C., respectively. Identity in each case was confirmed by comparison of the infrared spectrum with that reported in the literature (63).

Triethylamine was purchased in the highest available purity and then refluxed over calcium hydride and distilled; the fraction collected was in the range 88.5-89.5°C./759 mm.

Phosphorus compounds were obtained commercially and in most cases were used as received. Many oxygen- and moisture-sensitive phosphines deteriorated with age once the container had been opened and these were vacuum distilled prior to using.

Solvents. Reagent grade solvents were used throughout. Where drying was required the usual drying procedures were used. The dry solvents were then distilled. Every effort was made to avoid absorption of moisture by these solvents.

Nitrogen. Nitrogen was used to provide a dry, inert atmosphere wherever it was called for. Water-pumped nitrogen was purified by passing the gas over metallic copper turnings at 400°C. to remove oxygen and then through anhydrous magnesium perchlorate to remove moisture.

Equipment

In addition to the usual laboratory glassware, several pieces designed to carry out small scale reactions in the absence of air and moisture were used. Ace Mini-Lab apparatus (Figure 7) is an example of such special equipment.

Transfers and handling under anhydrous conditions were facilitated by the use of a Lucite dry box in which was maintained a dry, nitrogen atmosphere, Figure 8. Manipulations were performed through a pair of Neoprene gloves and every effort was made to avoid unnecessary opening of the box. Several dishes of phosphorus (V) oxide were placed in each stage of the box to absorb moisture.

Most elemental analyses were performed by the Galbraith Micro-analytical Laboratories, Knoxville, Tennessee. Some nitrogen analyses, however, were performed with a Coleman nitrogen analyzer, Model 33.

Melting points were determined in sealed capillary tubes in a Thomas-Hoover melting point apparatus. Infrared spectra were obtained on a Perkin-Elmer Infracord Model 137 infrared spectrophotometer. Nuclear magnetic resonance spectra were obtained on a Varian High-Resolution Nuclear Magnetic Resonance Spectrometer, Model V-4300-2.

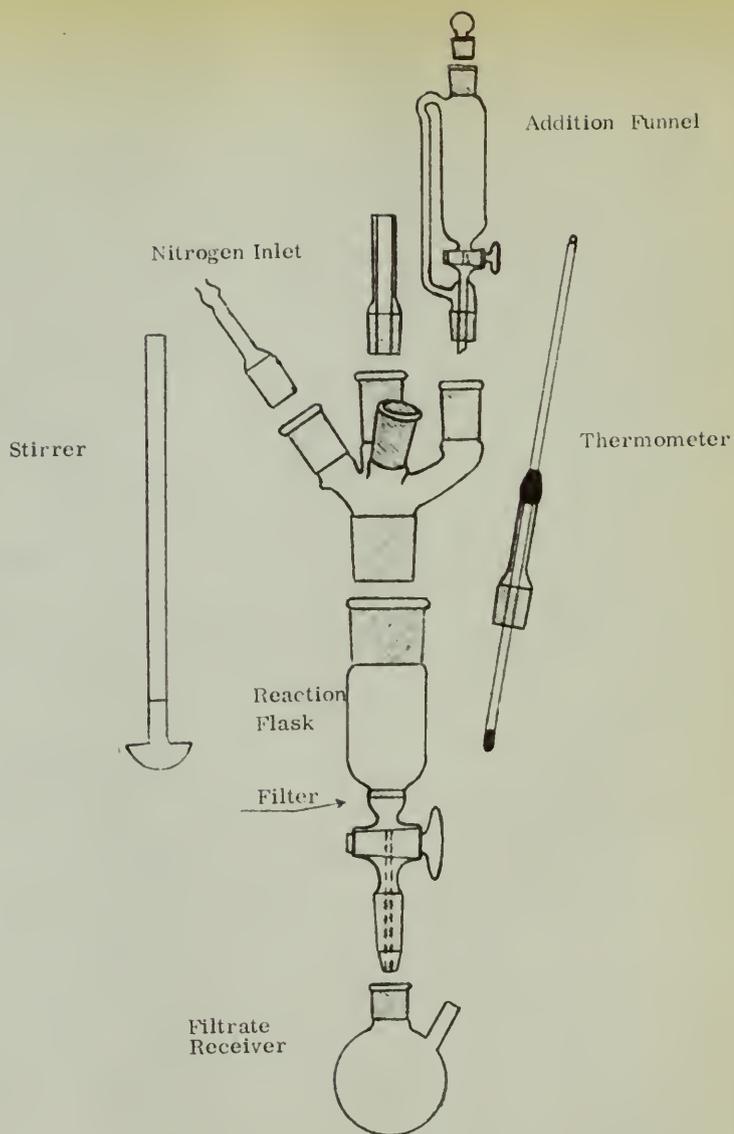


Figure 7. Mini-Lab Reaction Apparatus

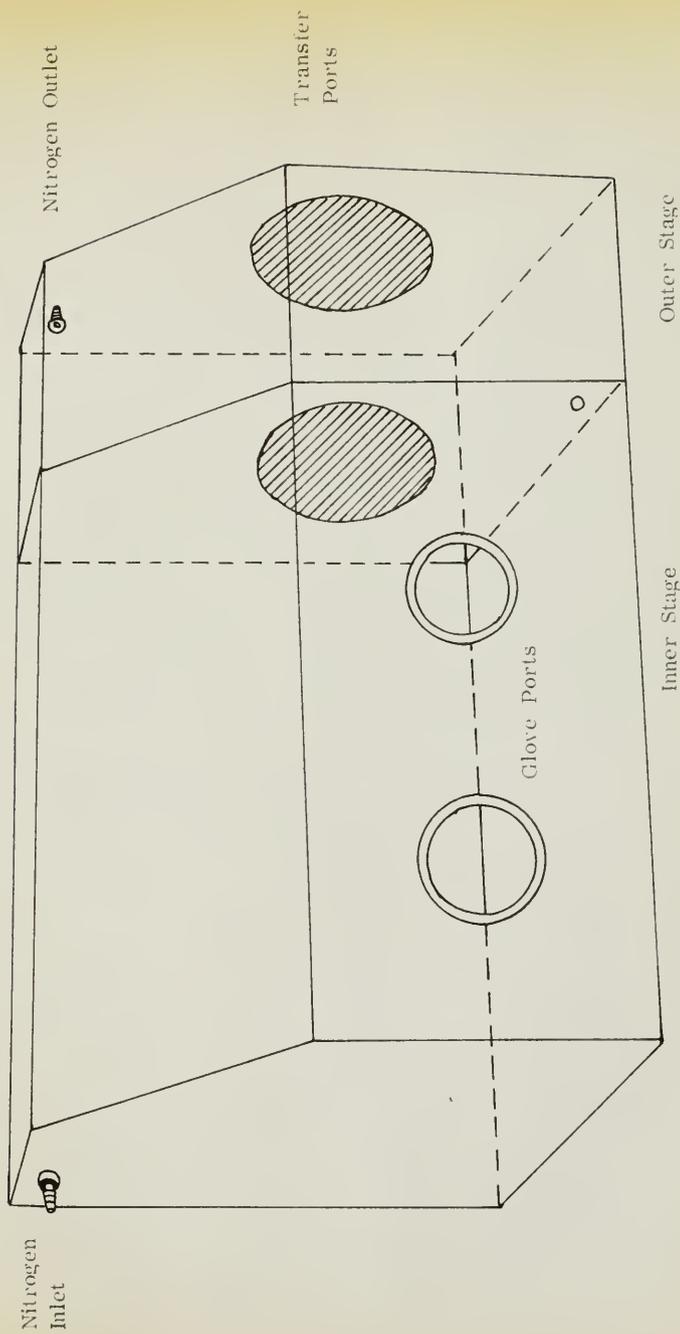


Figure 8. Dry Box (Three-Eighths Inch Lucite Construction)

Experiments with 1,1-dimethylhydrazine and chlorodiphenylphosphine

2,2-Dimethylhydrazinodiphenylphosphine. 2,2-Dimethylhydrazinodiphenylphosphine was synthesized by the hydrazinolysis of chlorodiphenylphosphine as shown below:



Similar solvolytic reactions are well known and have been used to prepare aminophosphines and other compounds in which it was desired to form a phosphorus-nitrogen covalent bond. However, this method had not been used previously to synthesize hydrazinophosphines. The nature of the reactants are such that moisture and oxygen must be avoided. It is also desirable to use a solvent in which the desired product is soluble, but from which the 1,1-dimethylhydrazinium salt will precipitate.

Fifty-five and one tenth g. (0.25 mole) chlorodiphenylphosphine was dissolved in 25 ml. dry benzene and added, with stirring and cooling, to a solution of 33 g. (0.55 mole) 1,1-dimethylhydrazine in 25 ml. benzene. The addition took four hours after which time the mixture was allowed to slowly warm to room temperature. The mixture was then stirred for an additional hour at room temperature to allow the precipitated crystals of 1,1-dimethylhydrazinium chloride to assume sufficient size for easy filtration.

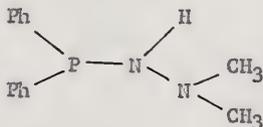
Filtration yielded, after washing successively with benzene and ether, 23.99 g. of a white, crystalline solid, m.p. 79-81°C. (literature value for 1,1-dimethylhydrazinium chloride, 81-82°C. (64)). This amount is 99.3 per cent of theory.

Evaporation of the filtrate at room temperature and reduced pressure gave 59.97 g. of white solid, m.p. 62-66°C. This solid was dissolved in 175 ml. dry hexane at 70°C. and the resulting solution was filtered. Upon cooling the solution to room temperature, crystals formed; these were collected and found to weigh 55.0 g. and melted at 65-67°C.

Sublimation of this product at 60°C./0.20 mm. gave long, prismatic crystals, m.p. 68.5-69.5°C. The overall yield was 51.5 g. (84.5 per cent of theory based on the equation presented above).

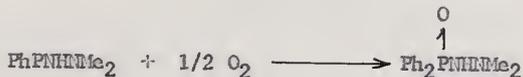
Analysis. Found: C, 68.65; H, 7.17; N, 11.29; P, 12.66. Calcd. for $C_{14}H_{17}N_2P$: C, 68.83; H, 7.02; N, 11.47; P, 12.68.

The infrared spectrum (Figure 9) and nuclear magnetic resonance spectrum (Figure 10) are consistent with the following structure:



2,2-Dimethylhydrazinodiphenylphosphine oxide. In order to further characterize 2,2-dimethylhydrazinodiphenylphosphine its oxide was prepared by three alternate routes: 1) atmospheric oxidation of the hydrazinophosphine, 2) oxidation of the hydrazinophosphine with activated manganese dioxide, and 3) the reaction of diphenylphosphinic chloride with 1,1-dimethylhydrazine.

1. Atmospheric oxidation.



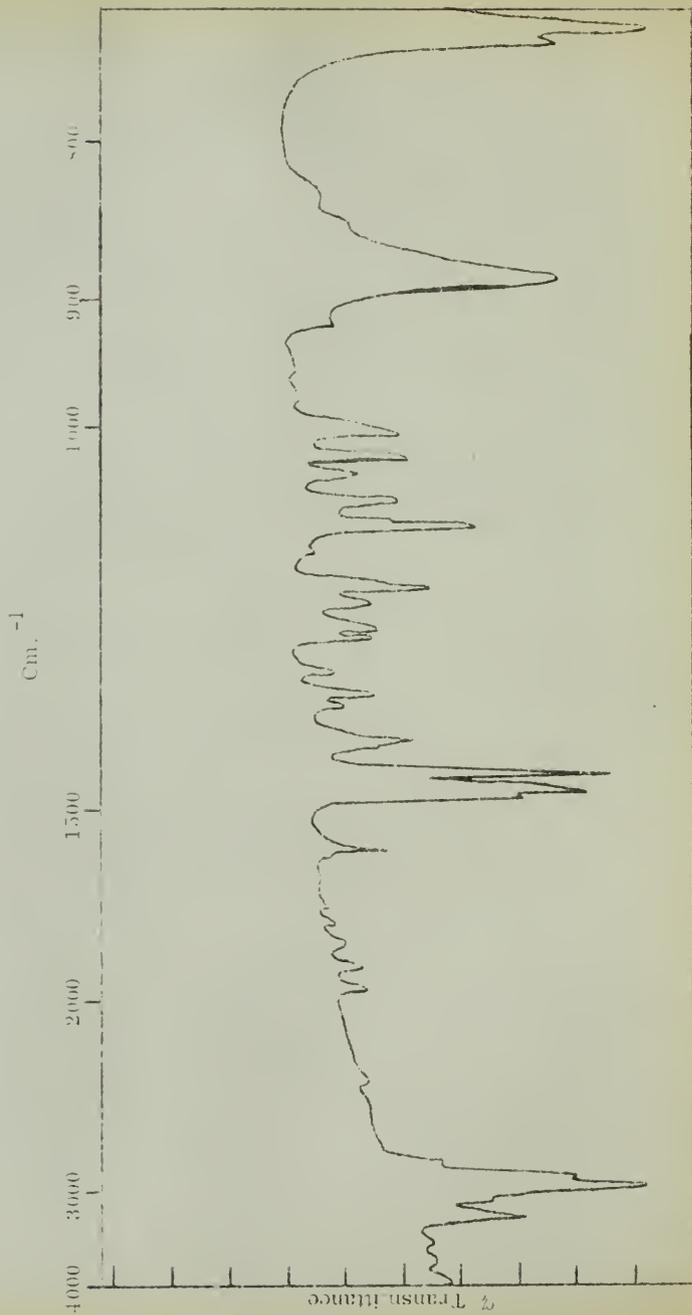


Figure 9. Infrared Spectrum of 2,2-Dimethylhydrazinobiphenylphosphine (Nu, of Mull)

Solvent: CDCl_3

Frequency: 56.4 mc.

Peak	Area	Position (ppm)	Type
A	10.2	-0.88	$-\text{C}_6\text{H}_5$
B	1.0	3.29	$-\text{NH}$
C	6.2	4.07	$-\text{CH}_3$

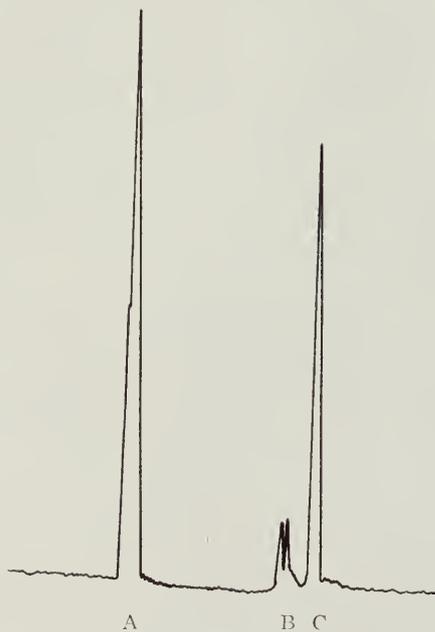


Figure 10. Proton Nuclear Magnetic Resonance Spectrum
of 2,2-Dimethylhydrazinodiphenylphosphine

A solution of 2.94 g. (0.012 mole) 2,2-dimethylhydrazinodiphenylphosphine in 50 ml. benzene was heated overnight while a stream of dry air was passed over the solution. Upon complete evaporation of the benzene there was obtained a white, crystalline mass and a dark oil. The crystals were collected and recrystallized from warm benzene and then sublimed at 160°C./0.32 mm.; 0.94 g. (30 per cent of theoretical, based on 2,2-dimethylhydrazinodiphenylphosphine) of a white, crystalline solid, m.p. 166.5-168.0°C. resulted.

2. Oxidation with activated MnO₂.



Two and ninety-four hundredths grams (0.012 mole) 2,2-dimethylhydrazinodiphenylphosphine in 50 ml. benzene was heated at 50°C. with 4.1 g. (0.72 mole) activated manganese dioxide (65) for 12 hours. The mixture was then filtered and upon evaporation of the benzene there was obtained a crop of white crystals. This solid was recrystallized from benzene and then sublimed at 160°C./0.30 mm. to give 1.60 g. of a white, crystalline solid, m.p. 166.5-168.5°C. (45 per cent yield, based on 2,2-dimethylhydrazinodiphenylphosphine).

3. Reaction of diphenylphosphinic chloride with 1,1-dimethylhydrazine.



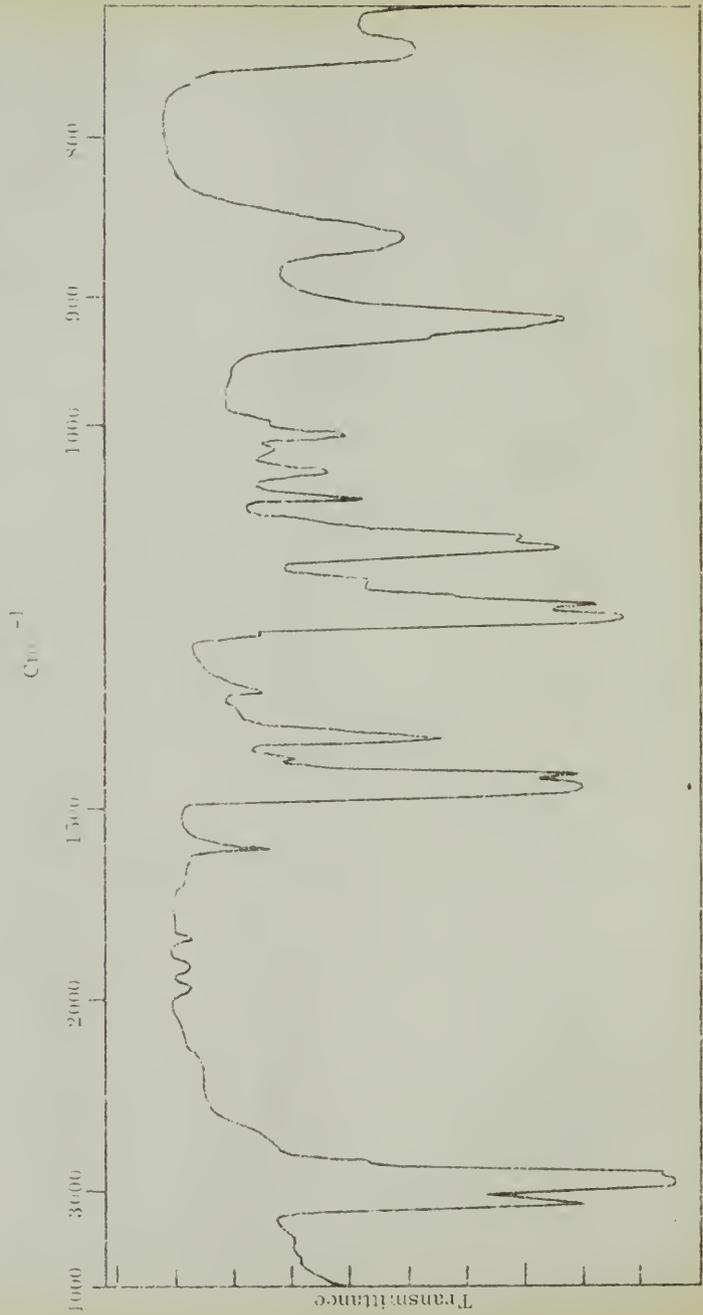
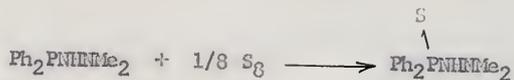


Figure 11. Infrared Spectrum of: 2,2-Dimethylhydrazinodiphosphine Oxide (Nujol Mull)

2,2-Dimethylhydrazinodiphenylphosphine sulfide.

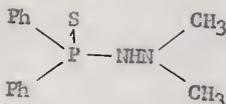


Three and forty-seven hundredths grams (0.0142 mole) of 2,2-dimethylhydrazinodiphenylphosphine was dissolved in 50 ml. dry benzene and added to 0.48 g. (0.015 mole) of finely divided sulfur in a small flask. The sulfur dissolved easily as the solution was warmed to 60°C. The solution was heated at 60°C. for 30 minutes and then cooled to room temperature; no solid appeared on cooling.

Upon evaporation of the solvent a white solid, m.p. 87-96°C., was obtained. Recrystallization from 1:1 benzene:n-hexane gave 3.59 g. (92 per cent of theory, based on the above reaction) of white crystals, m.p. 95.5-97.0°C.

Analysis. Found: C, 60.67; H, 6.20; N, 10.14; P, 11.21; S, 11.60. Calcd. for $\text{C}_{14}\text{H}_{17}\text{N}_2\text{PS}$: C, 60.85; H, 6.41; N, 10.26; P, 11.45; S, 11.41.

The n.m.r. and infrared (Figure 12) spectra were consistent with the structural formula below:



2,2-Dimethylhydrazinomethylidiphenylphosphonium iodide.



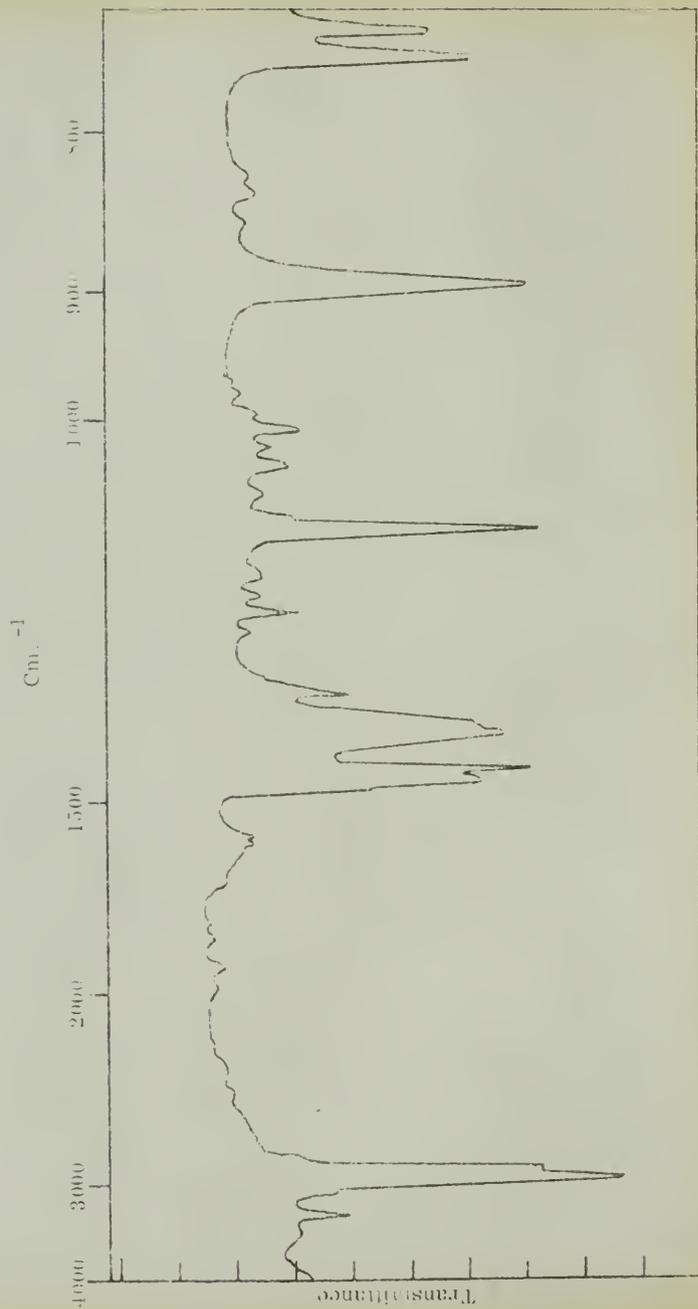


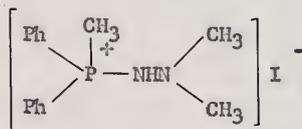
Figure 12. Infrared Spectrum of 2,2'-Bis[ethyldiazinodipropenyl]phosphine Sulfide (Nujol Mull)

One and seventy-two hundredths g. (0.00704 mole) 2,2-dimethylhydrazinodiphenylphosphine and 1.0 g. (0.00704 mole) methyl iodide were dissolved in 25 ml. dry ether and the solution was stirred at 25°C. overnight. At the end of this time a solid was filtered from the solution and dried at room temperature and reduced pressure. The white solid weighed 2.71 g. (100 per cent yield, based on the above equation) and melted at 156-158°C. An attempt to sublime this material resulted in thermal decomposition at 160°C. The salt is soluble in absolute ethanol.

Analysis. Found: C, 46.85; H, 5.47; N, 7.10; P, 7.85. Calcd. for $C_{15}H_{20}N_2PI$: C, 46.65; H, 5.22; N, 7.25; P, 8.02.

A water-alcohol solution of this solid gives a positive iodide ion test, and iodine is liberated by the addition of nitric acid.

The infrared spectrum (Figure 13) is consistent with the structural formula:



The structure was further confirmed by basic aqueous hydrolysis to 1,1-dimethylhydrazine and methyldiphenylphosphine oxide. The oxide was identified by conversion to methyldiphenylphosphinic hydrogen carbonate.

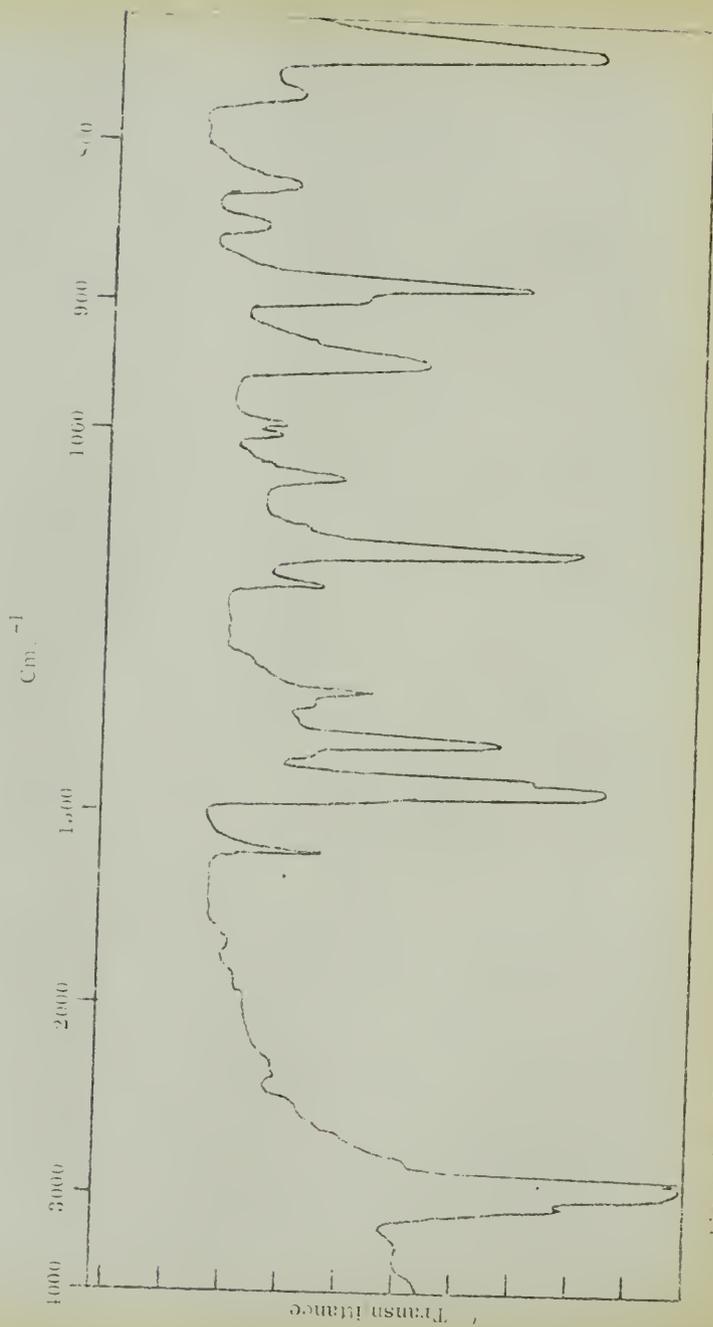
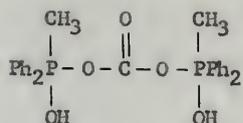


Figure 13. Infrared Spectrum of 2,2-Dimethylhydrazinomethyl(1-phenyl)phosphonium Ioxide (NuroI MuIf)

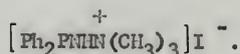
Hydrolysis of 2,2-dimethylhydrazinomethyldiphenylphosphoniumiodide.

Two grams of sodium hydroxide was added to 3 g. of 2,2-dimethylhydrazinomethyldiphenylphosphonium iodide in 25 ml. of 1:1 ethanol:water solution and the mixture was boiled for one hour. As the alcohol evaporated it was replaced with water. The vapor above the solution was tested for the presence of free base (1,1-dimethylhydrazine) with damp red litmus paper and for the presence of a reducing substance with a drop of potassium permanganate solution on a strip of filter paper. Both tests were positive.

An oil separated from the aqueous solution. The amount of oil was too small for distillation, but an infrared spectrum consistent with methyldiphenylphosphine oxide was obtained. The oil was treated with a solution of sodium carbonate at 90°C. for two hours and upon evaporation of the water a white solid residue was left. This was extracted with hot benzene and filtered. Evaporation of the filtrate gave one gram of a white solid, m.p. 107-109°C. This solid evolved carbon dioxide upon contact with a drop of hydrochloric acid. The literature value for the melting point of methyldiphenylphosphinic hydrogen carbonate, is 109-111°C. (66), and it is reported to liberate carbon dioxide upon contact with hydrochloric acid.



From the foregoing experimental evidence we can conclude that the alkylation of 2,2-dimethylhydrazinodiphenylphosphine with methyl iodide produces the hydrazinophosphonium salt rather than the hydrazinium salt indicated below:



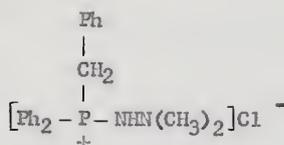
Attempted alkylation of 2,2-dimethylhydrazinomethyldiphenylphosphonium iodide with excess methyl iodide. Treatment of 2,2-dimethylhydrazinomethyldiphenylphosphonium iodide with excess methyl iodide in ether or toluene (heterogeneous reaction) gives quantitative recovery of starting materials. It is clear, therefore, that, under the conditions cited here, alkylation of 2,2-dimethylhydrazinomethyldiphenylphosphonium iodide does not occur.

Other hydrazinophosphonium salts. Samples of 2,2-dimethylhydrazinodiphenylphosphine were treated with various organic halides in an attempt to obtain additional information relevant to the ease of alkylation of the phosphine.

Reaction with benzyl chloride. Four and eight hundredths grams (0.0168 mole) 2,2-dimethylhydrazinodiphenylphosphine and 2.12 grams (0.0168 mole) benzyl chloride were dissolved in 50 ml. dry toluene and the mixture was refluxed at 110°C. for 12 hours.

Upon cooling to room temperature two liquid layers were observed. The toluene was removed and attempts were made to initiate

crystallization by cooling and by adding ether to the layer containing the desired product. No crystallization occurred and the product could not be purified by crystallization from absolute ethanol. The clear, yellow, viscous liquid gave a positive Cl^- test, however, and although the compound was not obtained pure, its infrared spectrum does indicate a salt-like structure which contains the bonds expected for 2,2-dimethylhydrazinobenzoyldiphenylphosphonium chloride



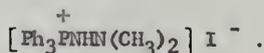
Reaction with carbon tetrachloride. Upon dissolving 2,2-dimethylhydrazinodiphenylphosphine in reagent grade carbon tetrachloride there forms in the yellow solution a faint precipitate which gradually disappears upon standing. Although no compound was isolated, there is the possibility that alkylation occurs according to the following equation:



Reaction with phenyl iodide. One gram 2,2-dimethylhydrazinodiphenylphosphine was mixed with excess phenyl iodide in dry ether and heated for one hour on the steam bath while the sample was protected from moisture with a drying tube. Several small crystals

formed in the liquid and these were washed with ether and dried in the air. The melting point was 162-175°C., and a nitric acid solution gave a positive I^- test.

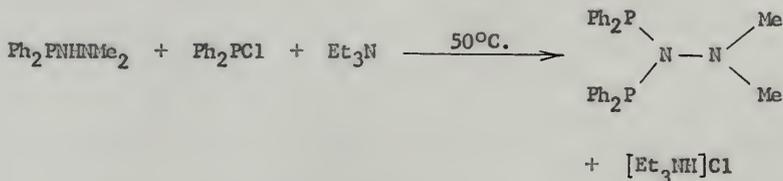
No suitable method of purification was found. Sublimation attempts resulted in thermal decomposition. The compound is thought to be 2,2-dimethylhydrazinotriphenylphosphonium iodide,



Reaction with β, β' -dibromoethyl ether. Two and forty-three hundredths g. (0.01 mole) 2,2-dimethylhydrazinodiphenylphosphine was reacted with a threefold excess of β, β' -dibromoethyl ether in toluene at 60°C. for 5 hours. A semi-solid which was not purified was the only observed product.

Synthesis of 1,1-bis(diphenylphosphino)-2,2-dimethylhydrazine.

An experiment designed to test whether chlorodiphenylphosphine would undergo hydrazinolysis by 2,2-dimethylhydrazinodiphenylphosphine resulted in the synthesis of 1,1-bis(diphenylphosphino)-2,2-dimethylhydrazine according to the following equation:



Three and fifty-four hundredths g. (0.0161 mole) chlorodiphenylphosphine and 3.62 g. (0.0358 mole) triethylamine were dissolved in 50 ml. dry toluene and to this was added quickly at room

temperature a solution of 3.84 g. (0.0161 mole) 2,2-dimethylhydrazino-phenylphosphine in 50 ml. toluene. There was no immediate evidence of reaction.

The temperature was slowly increased and at 50°C. a solid appeared in the solution. Above 50°C. the precipitation was copious. The mixture was stirred at 110°C. for one hour and filtered; the precipitate melted at 251-253°C. (literature value for triethylammonium chloride is 254°C.). Yield: 2.12 g. (96 per cent of theory, based on the above equation).

Evaporation of the filtrate gave 6.51 g. of a white solid, m.p. 126-133°C. An attempt at sublimation resulted in decomposition at 135°C. Recrystallization from dry n-heptane gave fine, white crystals, m.p. 129.5-132.5°C., in 76 per cent yield, based on the equation above.

Analysis. Found: C, 72.65; H, 5.98; N, 6.39; P, 14.56.

Calcd. for $C_{26}H_{26}N_2P_2$: C, 72.88; H, 6.12; N, 6.54; P, 14.46.

The n.m.r. spectra and infrared spectrum (Figure 14) are consistent with the proposed structure, but a small absorption peak at 1176 cm^{-1} in the infrared shows some oxygen (as P=O) as an impurity.

Chlorophosphination of triethylamine. Since, as in the synthesis described above, it has in several instances proved convenient to use triethylamine rather than an excess of the hydrazine as a hydrogen chloride acceptor, it was desirable to determine whether or not chlorodiphenylphosphine reacts directly with triethylamine.

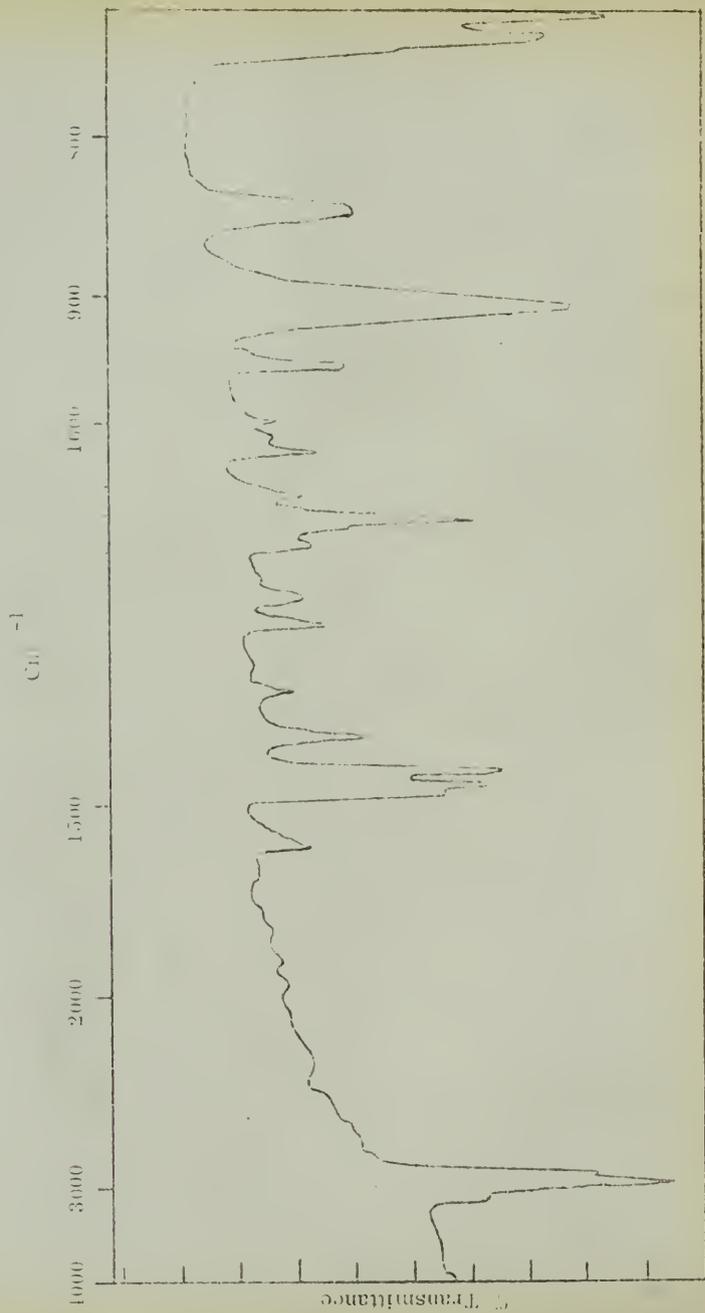


Figure 14. Infrared Spectrum of 1,1-Eis(diphenylphosphino)-2,2-dimethylhydrazine (Nujol Mull)

In view of the fact that chloramine has been shown to react with tertiary phosphines in accordance with the equation (67)



it might be expected that chlorophosphines such as $(\text{C}_6\text{H}_5)_2\text{PCl}$ would react with tertiary amines according to the following equation:



In an experiment designed to test whether or not chlorophosphination of triethylamine occurs under the conditions usually employed in the hydrazinolysis of chlorodiphenylphosphine 5.46 g. (0.054 mole) triethylamine was dissolved in 50 ml. anhydrous ether and added to 11.90 g. (0.054 mole) chlorodiphenylphosphine in 50 ml. ether. An immediate cloudiness appeared in the solution which persisted throughout a 30 minute reflux at 40°C.

Filtration gave 0.63 g. of a white solid, m.p. 254-255°C., which was completely water soluble. A mixed melting point determination with an authentic sample of triethylammonium chloride melted at 253-254°C.; the infrared spectrum of this solid is identical with that of triethylammonium chloride.

Evaporation of the ether and triethylamine from the filtrate at reduced pressure gave a yellow viscous liquid which was distilled at 105-107°C./0.17 mm. and shown to be chlorodiphenylphosphine by its infrared spectrum.

It may, therefore, be concluded that chlorophosphination of triethylamine with chlorodiphenylphosphine does not occur under the conditions employed here for the hydrazinolysis of chlorodiphenylphosphine.

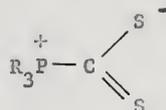
It should be noted that a little triethylammonium chloride resulted from the reaction mixture, showing that although all reagents had been previously distilled and dried, some hydrolysis had occurred. It was later found to be possible to avoid the formation of triethylammonium chloride upon mixing chlorodiphenylphosphine and triethylamine by performing all transfers in the dry box. For the usual bulk reaction, however, it is unnecessary to take the extra care to avoid this small amount of hydrolysis as it lowers the yield by only a fraction of a per cent.

Reaction of 2,2-dimethylhydrazinodiphenylphosphine with carbon disulfide. Five ml. reagent grade carbon disulfide was added to 1.97 g. (0.0807 mole) 2,2-dimethylhydrazinodiphenylphosphine in 10 ml. anhydrous ether. A deep red color developed immediately and slowly faded to yellow as the solution was evaporated at 40°C. over a five hour period.

Upon standing overnight, large, white crystals appeared in the solution. These were collected and washed with hexane and melted at 140.5-141.5°C. The yield was 82 per cent of theory, assuming the 2,2-dimethylhydrazinodiphenylphosphine reacted with the carbon disulfide in a 1:1 ratio. The analysis corresponds to $(C_6H_5)_2PNHN(CH_3)_2 \cdot CS_2$: Found: C, 56.09; H, 5.55; N, 8.69; P, 9.46; S, 20.17. Calcd. for $C_{15}H_{17}N_2PS_2$: C, 56.23; H, 5.35; N, 8.74; P, 9.67; S, 20.01.

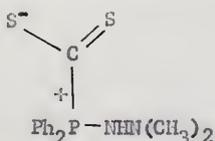
It was found that if the white, crystalline product of this reaction is redissolved in carbon disulfide, the red color appears once more.

The literature describes the interaction of tertiary phosphines with carbon disulfide, and there are reported compounds of the type



which are red, crystalline solids (55,68). The structures of these compounds have been confirmed by X-ray diffraction analysis (69) and it is well-known that the compounds contain a P-C bond and no formal P-S bonds. The red color is thought to arise as a result of the Zwitterion-type structure.

Since a red color develops in the interaction of 2,2-dimethylhydrazinodiphenylphosphine with excess carbon disulfide, it appears that a Zwitterion complex is the initial product of the reaction:



As the reaction proceeds, however, the color fades as the amount of carbon disulfide is decreased. The final product is a white solid and has an infrared spectrum (Figure 15) which is complex, but shows no absorption in the region assigned to the N-H bond. The N-N absorption has been shifted to a higher frequency which indicates a change in one of the substituents on the nitrogen atom attached to the phosphorus; the $-\text{N}(\text{CH}_3)_2$ group appears to be intact. A weak absorption is evident in the S-H region. The monosubstituted phenyl

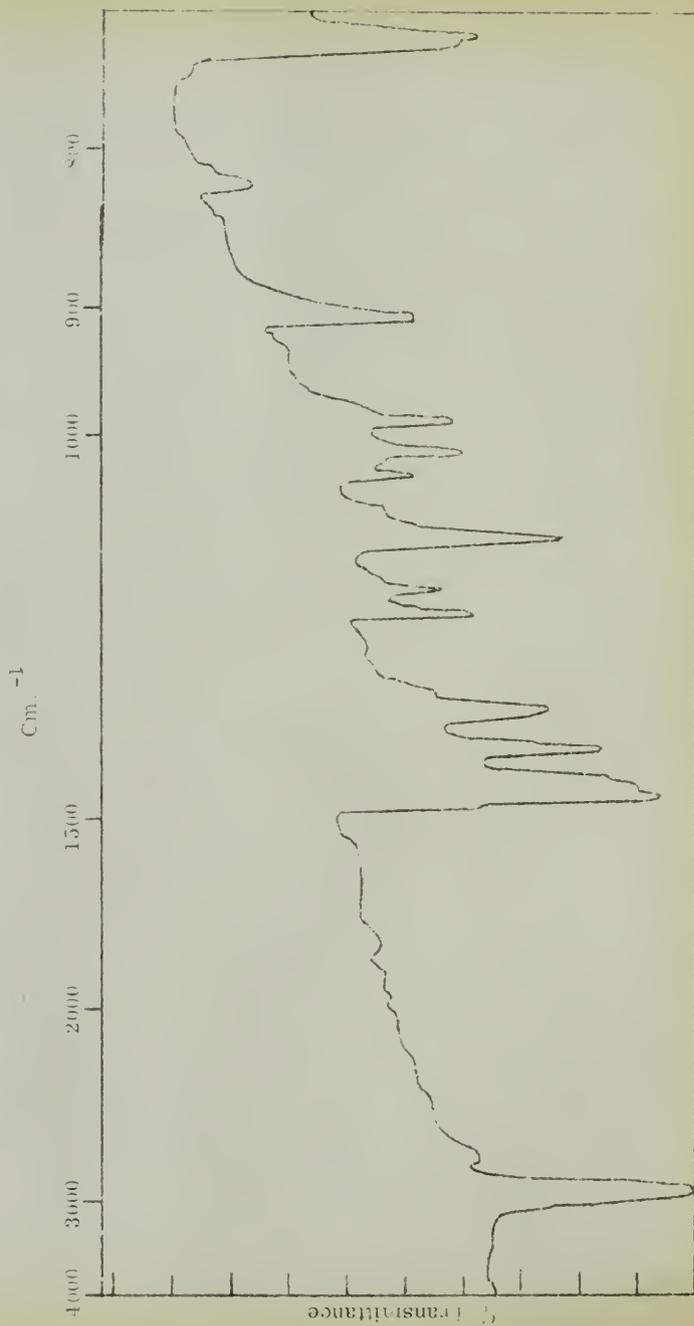
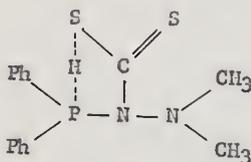


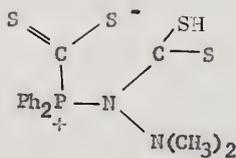
Figure 15. Infrared Spectrum of the Product of the Reaction of 2,2-Dimethylhydrazinooxiphenylphosphine with Carbon Disulfide (Nujol Mull)

group peaks are unchanged and the P-phenyl absorption has not been shifted at all. The structure best fitting the infrared data is drawn below:



The proton nuclear magnetic resonance spectrum is in general agreement with this structure. Four peaks are observed, none of which is the characteristic N-H close doublet which is observed in 2,2-dimethylhydrazinodiphenylphosphine. The peaks assigned as phenyl protons and methyl protons agree with the areas expected for the structure given above. The remaining two peaks are of unequal area and are presumed to arise from 1) the S-H proton and 2) the proximity of the S-H proton to the ^{31}P atom, which is an odd nucleon and with which ^1H will interact by spin-spin coupling.

The fact that a red color develops on dissolving this material in carbon disulfide may indicate that the phosphorus atom is still available for loose coordination in excess carbon disulfide, and gives a molecular complex as shown below.



Treatment of 2,2-dimethylhydrazinodiphenylphosphine oxide with carbon disulfide resulted in no reaction.

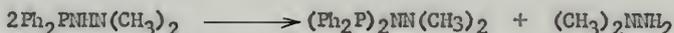
Pyrolytic condensation of 2,2-dimethylhydrazinodiphenylphosphine. It has been observed that when a sample of 2,2-dimethylhydrazinodiphenylphosphine is purified by sublimation, there sometimes is

left behind in the pot of the sublimation apparatus a yellow, resinous material. On these occasions there is also found in the cold trap used to protect the vacuum pump a small amount of a volatile liquid. Infrared analysis and vapor phase chromatography data indicate that this liquid contains dimethylamine and 1,1-dimethylhydrazine.

Dimethylamine can be produced by a thermal decomposition which produces the phosphonitrilic system,



and 1,1-dimethylhydrazine can be one of the products when 1,1-bis-(diphenylphosphino)-2,2-dimethylhydrazine is also a pyrolytic condensation product:



It should be noted that only a small amount of this solid, resinous material is observed after sublimation of 2,2-dimethylhydrazinodiphenylphosphine, but a suggestion for further work would be to investigate these reactions on a larger scale and identify with certainty the reaction products.

Hydrolysis of 2,2-dimethylhydrazinodiphenylphosphine. A sample of 2,2-dimethylhydrazinodiphenylphosphine was treated with 0.1 N HCl with the result that both 1,1-dimethylhydrazine and diphenylphosphinic acid (m.p. 191-193°C.) were isolated in high yield from the product mixture. The diphenylphosphinic acid was filtered from the solution and the 1,1-dimethylhydrazine was distilled from the filtrate which was made basic by the addition of NaOH solution.

Hydrolysis by atmospheric moisture was found to be a minor problem with 2,2-dimethylhydrazinodiphenylphosphine.

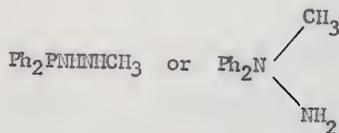
Experiments with methylhydrazine and chlorodiphenylphosphine

Reaction of methylhydrazine with chlorodiphenylphosphine. Ten and four tenths g. (0.0472 mole) chlorodiphenylphosphine was dissolved in 35 ml. dry ether and added to 4.35 g. (0.0945 mole) methylhydrazine (redistilled and dried over calcium hydride) in 40 ml. dry ether. The addition took four hours and was performed with cooling and stirring under a nitrogen atmosphere. No precipitation occurred at 0°C., but upon warming the mixture to 25°C. solid appeared and the mixture was stirred at 25°C. to allow the reaction to proceed to completion.

Filtration gave 3.71 g. methylhydrazinium chloride (theoretical is 3.88 g., based on chlorodiphenylphosphine), and 9.57 g. of a yellow, viscous liquid which did not contain chlorine, as evidenced by a silver nitrate test on a small portion dissolved in dilute nitric acid. No crystallization could be induced in the liquid and no way was found to effect purification.

Analysis. C, 67.55; H, 6.46; N, 11.96; P, 14.34. Calcd. for $C_{13}H_{15}N_2P$: C, 67.81; H, 6.57; N, 12.17; P, 13.45.

The reaction product may have either of two forms.



The n.m.r. spectra indicate that a mixture of both these species is present in the product, but the data are too complex to indicate the

relative percentages of the constituents. The infrared spectrum contains all the expected absorption frequencies, but is of little value in determining per cent composition.

An attempt to vacuum distill the product resulted in thermal decomposition. A liquid fraction was collected in the range 98-99°C./0.36 mm.; however, the bulk of the product remained in the distilling flask as a resinous, amber-colored solid.

Extrapolation of the boiling point at reduced pressure to the normal boiling point of the liquid on a temperature-vapor pressure nomograph gave ca. 175°C./760 mm. (diphenylphosphine boils at 230°C. per 760 mm. (32).

Analysis. Found: C, 77.42; H, 6.22; N, 0.25; P, 15.88.
Calcd. for $(C_6H_5)_2PH$: C, 77.41; H, 5.95; N, 0.00; P, 16.64.

The molecular weight (cryoscopically, in benzene) is 185.
Calcd. for diphenylphosphine: 186.2.

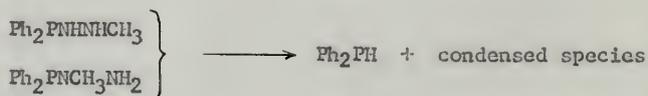
A methyl iodide derivative, prepared according to the equation



has a m.p. 241°C.

The infrared spectrum (Figure 16) is consistent with the structure for diphenylphosphine and contains a very prominent absorption peak at 2295 $cm.^{-1}$, which is characteristic for the P-H bond.

The thermal decomposition of the product mixture apparently is according to the following equation:



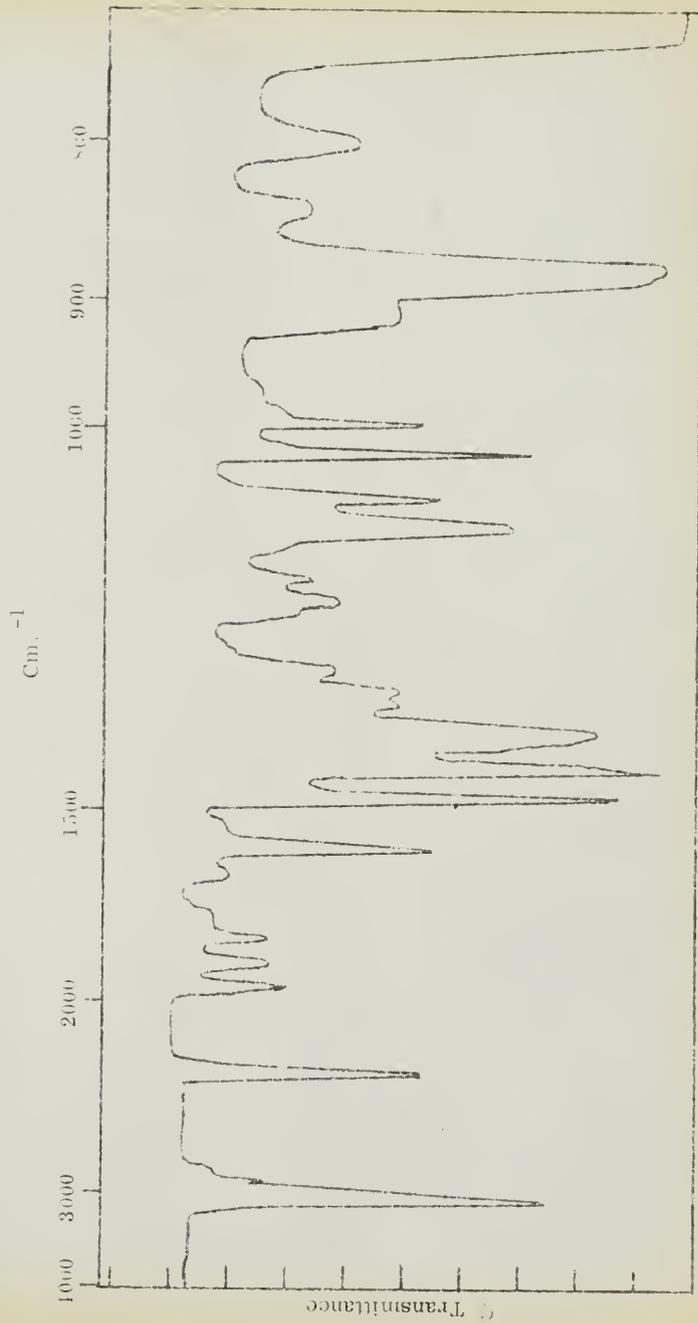


Figure 16. Infrared Spectrum of Diphenylpicosiline (Cell)

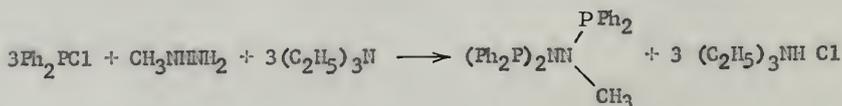
An attempt was made to separate the two components from each other by reaction with benzaldehyde, but the only isolated product was methylbenzylidenehydrazine, $C_6H_5CH=N-NHCH_3$, m.p. $178-179^{\circ}C$. (literature value $179^{\circ}C$.). Apparently the water produced in hydrazone formation hydrolyzed the P-N bond in the product.

No separation was made on the residue from the thermal decomposition and the analytical results did not agree with any single compound. The infrared spectrum was highly opaque, which is characteristic of polymeric materials.

Reaction of methylhydrazinodiphenylphosphine with sulfur. The mixture of methylhydrazinodiphenylphosphines produced in the reaction of chlorodiphenylphosphine with methylhydrazine was reacted with a small amount of finely divided sulfur in benzene solution with the result that hydrogen sulfide evolved and a dark gum was produced from which no product was isolated.

Reaction of methylhydrazinodiphenylphosphine with carbon disulfide. Upon dissolving the methylhydrazinodiphenylphosphine mixture in carbon disulfide there was no immediate evidence of reaction, however, over a 12 hour period hydrogen sulfide evolved, and upon removal of the solvent a dark gum remained from which no pure material was isolated.

Synthesis of 1,1,2-tris(diphenylphosphino)methylhydrazine.



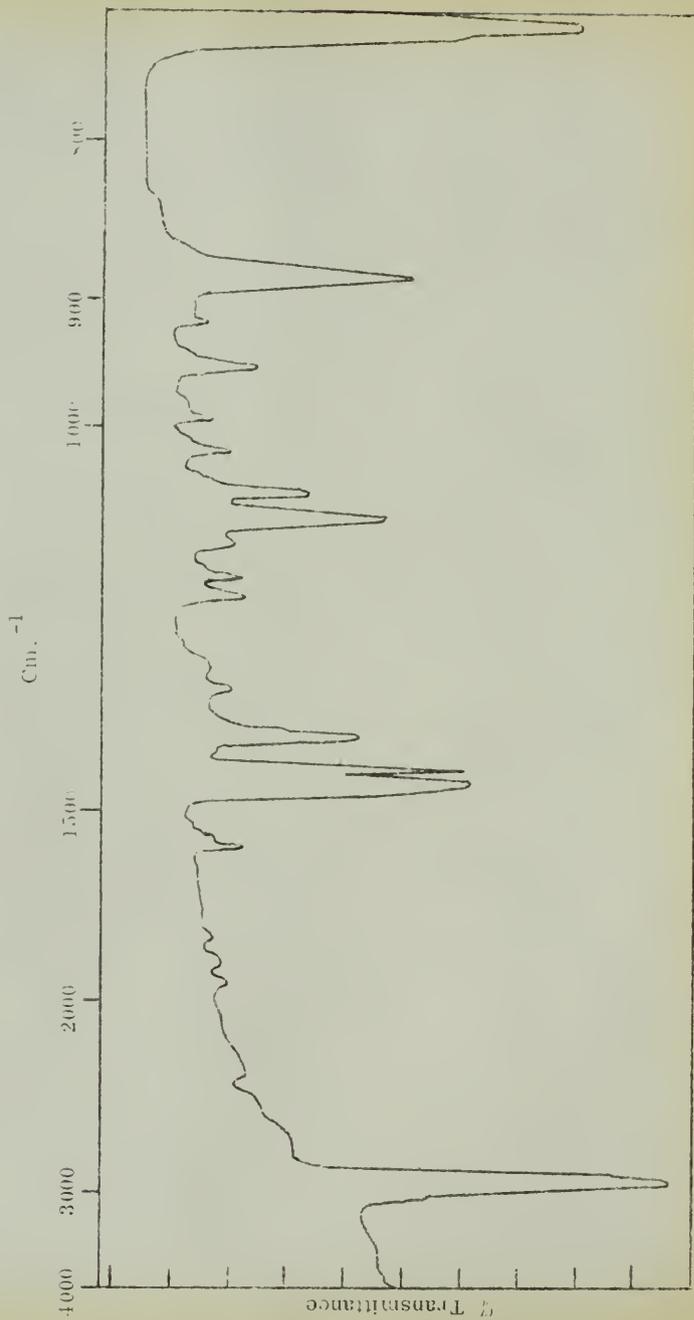
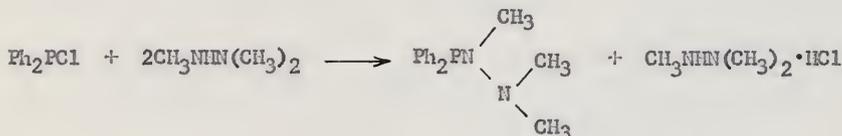


Figure 17. Infrared Spectrum of 1,1,2-Tris(diphenylphosphino)methylhydrazine (Nujol Mull)

No difficulty was experienced in handling this material in contact with the atmosphere, and a sample left out in the air for several hours underwent no detectable change.

Experiments with trimethylhydrazine and chlorodiphenylphosphine

The synthesis of 1,2,2-trimethylhydrazinodiphenylphosphine.

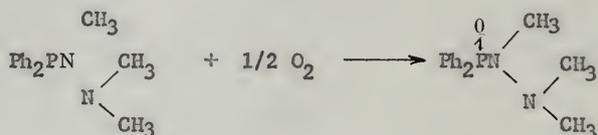


Eleven g. (0.05 mole) chlorodiphenylphosphine was dissolved in 20 ml. dry benzene and added slowly with stirring and cooling (to 0°C.) to 7.5 g. (0.1 mole) 1,1,2-trimethylhydrazine in 20 ml. dry benzene. The addition took 2-1/2 hours and at the end of this period little precipitate was observed in the reaction mixture. Additional precipitate appeared when the mixture was heated to 50°C. and stirred for one hour.

Filtration of the mixture gave 5.40 g. (98 per cent of theory based on chlorodiphenylphosphine) 1,1,2-trimethylhydrazinium chloride, m.p. 54-56°C. Evaporation of the solvent in vacuo at room temperature gave a clear, viscous liquid. No crystallization could be induced and vacuum distillation resulted in decomposition.

No characterization was attempted. Instead, the oxide was prepared as a derivative.

Atmospheric oxidation of 1,1,2-trimethylhydrazinodiphenylphosphine.

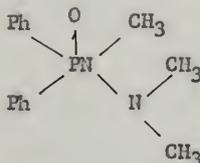


Four and three tenths g. of the liquid product of the above reaction was dissolved in 40 ml. benzene and exposed to dry air for four days. At the end of this time much of the benzene had evaporated and the flask contained long, white crystals imbedded in a yellow, viscous liquid. The crystals were collected and washed with a 1:1 benzene: *n*-hexane mixture. The m.p. was 139-162°C.; recrystallization from hot *n*-hexane gave a cleaner product, m.p. 159-163°C., and sublimation at 160°C./0.17 mm. gave 2.9 g. of a product which melted at 164.5-166.5°C. (63 per cent of theory).

Analysis. Found: C, 65.52; H, 6.92; N, 10.08; P, 11.03.

Calcd. for $\text{C}_{15}\text{H}_{19}\text{PN}_2\text{O}$: C, 65.68; H, 6.98; N, 10.22; P, 11.29.

The infrared (Figure 13) and n.m.r. spectra were consistent with the structural formula



This experiment serves to further confirm the identity of the product of the reaction between chlorodiphenylphosphine and 1,1,2-trimethylhydrazine.

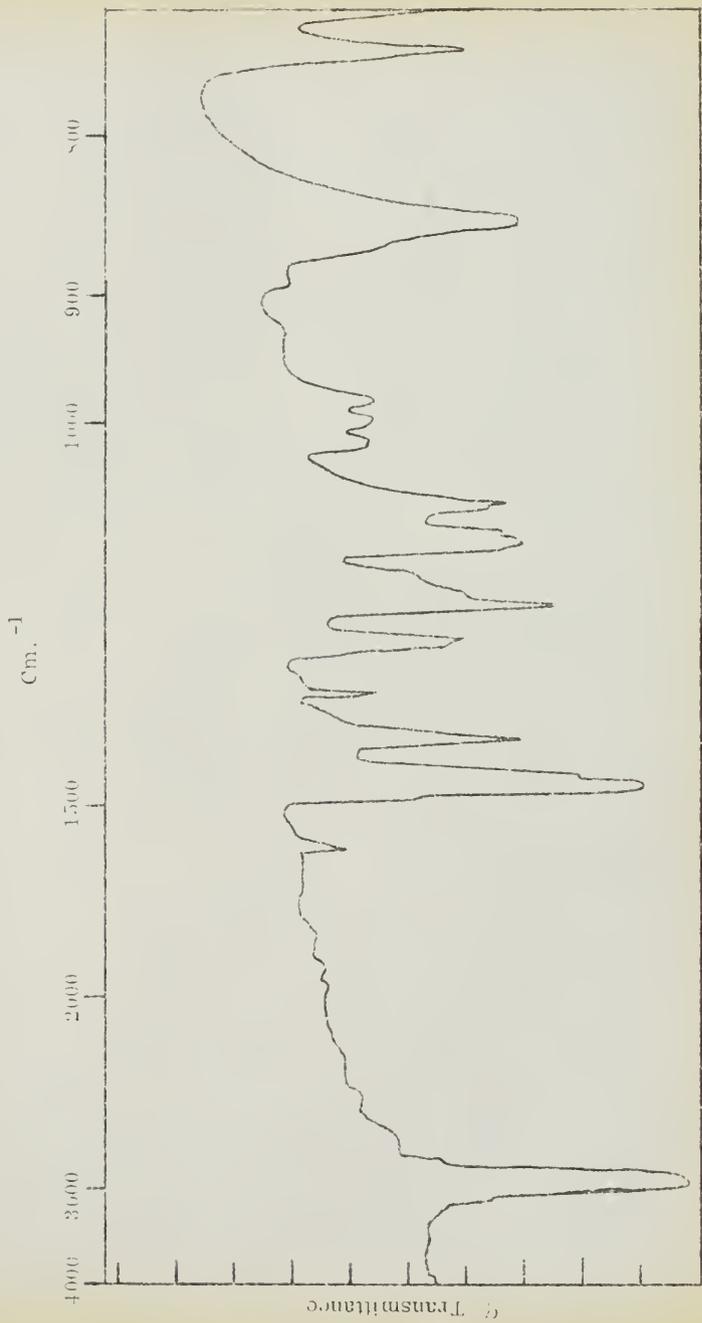
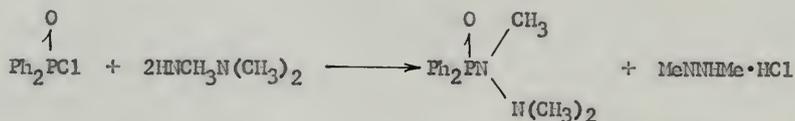


Figure 1s. Infrared Spectrum of 1, 2, 2-Trimethylhydrazinodiphenylphosphine Oxide (Nujol Mull)

Reaction of 1,1,2-trimethylhydrazine with diphenylphosphinic chloride.



Eight and fifteen hundredths g. (0.11 mole) 1,1,2-trimethylhydrazine was dissolved in 25 ml. dry benzene and added to 11.83 g. (0.05 mole) chlorodiphenylphosphine in 25 ml. benzene at 0°C. with stirring. There was no evidence of reaction at 0°C., but the reaction proceeded rapidly at 45°C., as evidenced by precipitation. The mixture was warmed to 60°C. for one hour and filtered to give 13.4 g. of white solid on the filter (theoretical is 5.55 g., based on the above reaction). Evaporation of the filtrate gave 6.15 g. of a gummy solid. After repeated attempts at purification by recrystallization and sublimation, attempts at purification were abandoned; most of the material decomposed on heating in solution or in the sublimation apparatus.

The precipitate from the filtration was heated in cyclohexane in an attempt to recover some of the product which had evidently been only partly soluble in the benzene and which had remained with the 1,1,2-trimethylhydrazinium chloride on the filter. The resulting mixture was filtered to give 5.49 g. 1,1,2-trimethylhydrazinium chloride, m.p. 54-56°C., and upon cooling the filtrate there was obtained 6.2 g. of fine, white crystals, m.p. 165.0-166.5°C. (45.2 per cent yield, based on the above equation).

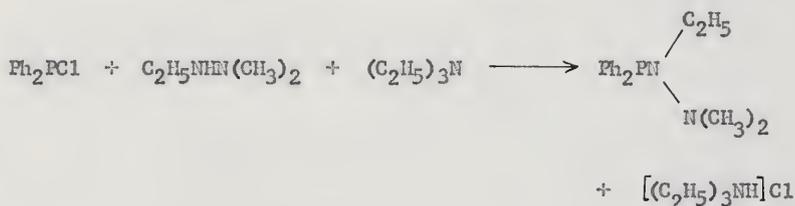
The infrared spectrum of this material was identical with that of the atmospheric oxidation product of the liquid obtained from the

reaction of chlorodiphenylphosphine and 1,1,2-trimethylhydrazine. A mixed melting point determination of these products melted at 165-166°C.

This experiment serves to confirm the identity of 1,2,2-trimethylhydrazinodiphenylphosphine oxide.

Experiments with 1-ethyl-2,2-dimethylhydrazine and chlorodiphenylphosphine

1-Ethyl-2,2-dimethylhydrazinodiphenylphosphine.



Six and seventeen hundredths g. (0.07 mole) 1-ethyl-2,2-dimethylhydrazine in 20 ml. dry benzene was added to a solution of 15.44 g. (0.07 mole) chlorodiphenylphosphine and 7.23 g. (0.0715 mole) triethylamine in 50 ml. benzene. There was no evidence of reaction at 5°C., but precipitation occurred as the solution was warmed to 35-40°C. The mixture was stirred at 40°C. for 3-1/2 hours and filtered to give 9.15 g. (95 per cent of theory, based on the equation above) triethylammonium chloride, m.p. 253-255°C.

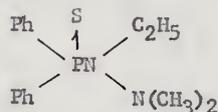
A viscous, straw-colored liquid was obtained upon evaporating the solution at room temperature and reduced pressure. No purification was attempted, but a negative test for chloride ion was obtained on a small portion dissolved in dilute nitric acid.

erlenmeyer flask. The mixture was warmed to 80°C. and allowed to boil for three hours after which the benzene was allowed to evaporate, yielding 3.87 g. (81.4 per cent of theory) of white crystals, m.p. 124.0-126.5°C.

Recrystallization from acetone gave long, highly refractive crystals, m.p. 126.5-127.5°C. No loss was suffered handling this material in air.

Analysis. Found: C, 63.30; H, 7.09; N, 9.10; P, 10.34; S, 10.62. Calcd. for $C_{16}H_{21}N_2PS$: C, 63.13; H, 6.95; N, 9.20; P, 10.18; S, 10.53.

The n.m.r. spectra, run in $CDCl_3$, and the infrared spectrum (Figure 19) were both consistent with this structural formula:



This experiment serves to further characterize 1-ethyl-2,2-dimethylhydrazinodiphenylphosphine.

Reaction of 1-ethyl-2,2-dimethylhydrazinodiphenylphosphine with methyl iodide. A threefold excess of methyl iodide was added to a benzene solution of 2.49 g. (0.0089 mole) 1-ethyl-2,2-dimethylhydrazinodiphenylphosphine. The solution rapidly became cloudy and a yellow oil separated within a matter of minutes.

Addition of ether to the gum produced some crystallization within a semisolid matrix. The crystals were separated from the gum and washed with benzene; they rapidly discolored from yellow to a dark brown upon exposure to air, but turned white upon heating to the melting point, 182-190°C.

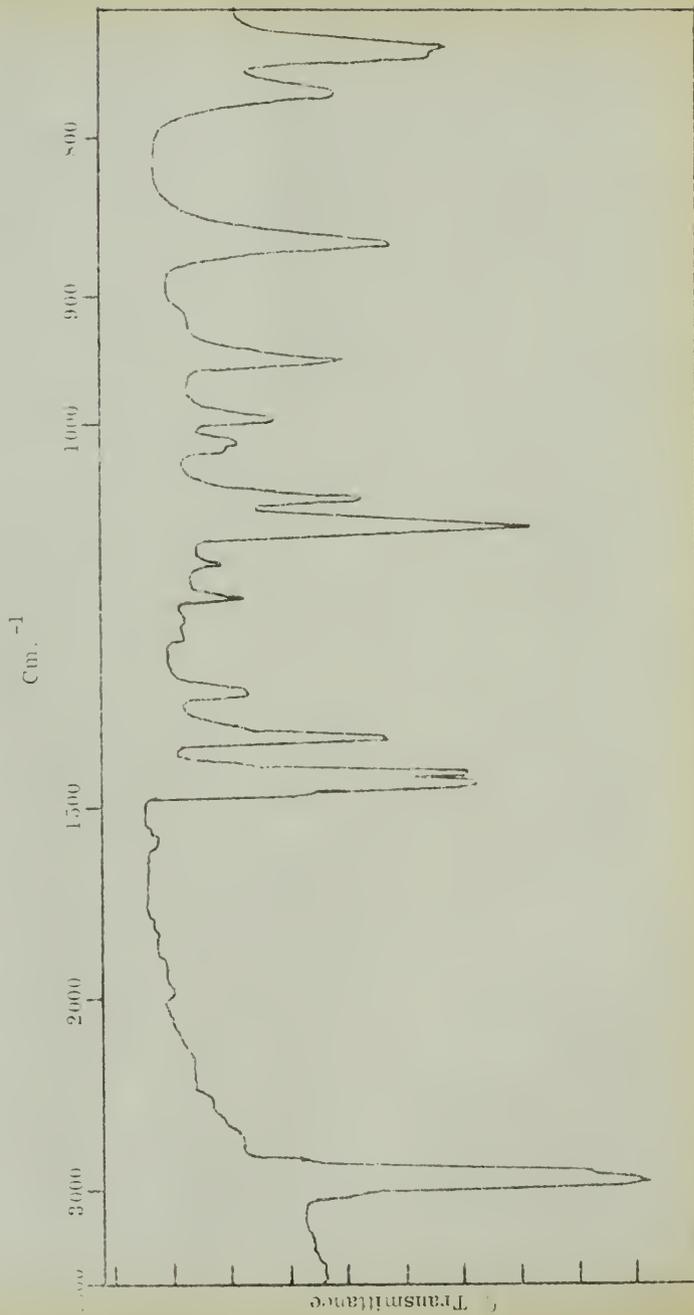
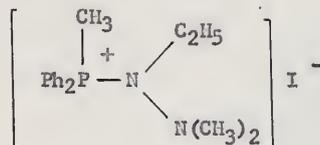
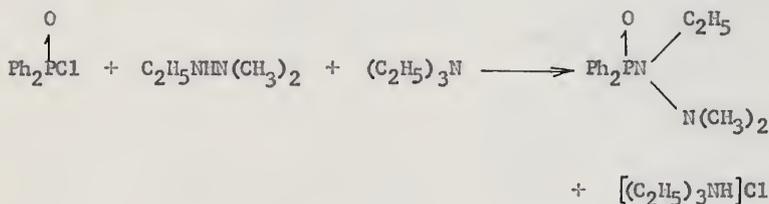


Figure 19. Infrared Spectrum of 1-Ethyl-2,2-(dimethylhydrazino)di(phenylphosphine) sulfide (Nujol Mull)

No purification method was found. The infrared spectrum was very poor, but indicated a salt-like structure by comparison with other spectra of phosphonium salts. The suggested structural formula is given below:



Reaction of 1-ethyl-2,2-dimethylhydrazine with diphenylphosphinic chloride.



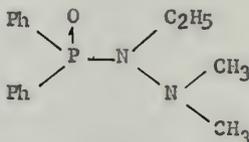
Six and seventeen hundredths g. (0.07 mole) 1-ethyl-2,2-dimethylhydrazine in 25 ml. dry benzene was added to a solution of 16.56 g. (0.07 mole) diphenylphosphinic chloride and 7.23 g. (0.0715 mole) triethylamine in 25 ml. benzene. There was no evidence of reaction at 0°C., but at 25°C. a precipitate formed in the solution. Precipitation was very slow at 25°C., and periodic checks of the benzene solution for the presence of chlorine revealed that the reaction had gone to completion after a period of two weeks. By this time the precipitate was voluminous and the larger octahedral crystals had grown to 1 cm. or more on an edge.

Filtration gave 8.97 g. (93.6 per cent of theory) triethylammonium chloride, m.p. 253-254°C., and 5.36 g. of white solid, m.p. 123-134°C., upon evaporation of the solvent in the filtrate. Sublimation of this solid gave a clear, highly refractive, crystalline solid which melted at 140.0-141.0°C.

Analysis. Found: C, 66.44; H, 7.24; N, 9.55; P, 10.89.

Calcd. for $C_{16}H_{21}N_2PO$: C, 66.65; H, 7.34; N, 9.72; P, 10.74.

The infrared (Figure 20) and n.m.r. spectra of the product are consistent with the structure



Reaction of 1-ethyl-2,2-dimethylhydrazinodiphenylphosphine oxide with methyl iodide. One g. samples of 1-ethyl-2,2-dimethylhydrazinodiphenylphosphine oxide were dissolved in benzene and toluene and heated with excess methyl iodide to 50°C. and 90°C., respectively, and allowed to evaporate to dryness. The product of both reactions was unreacted 1-ethyl-2,2-dimethylhydrazinodiphenylphosphine oxide and the absence of iodide ion was demonstrated by the addition of a drop of nitric acid which gave no reaction.

It is therefore concluded that alkylation of 1-ethyl-2,2-dimethylhydrazinodiphenylphosphine oxide with methyl iodide does not occur.

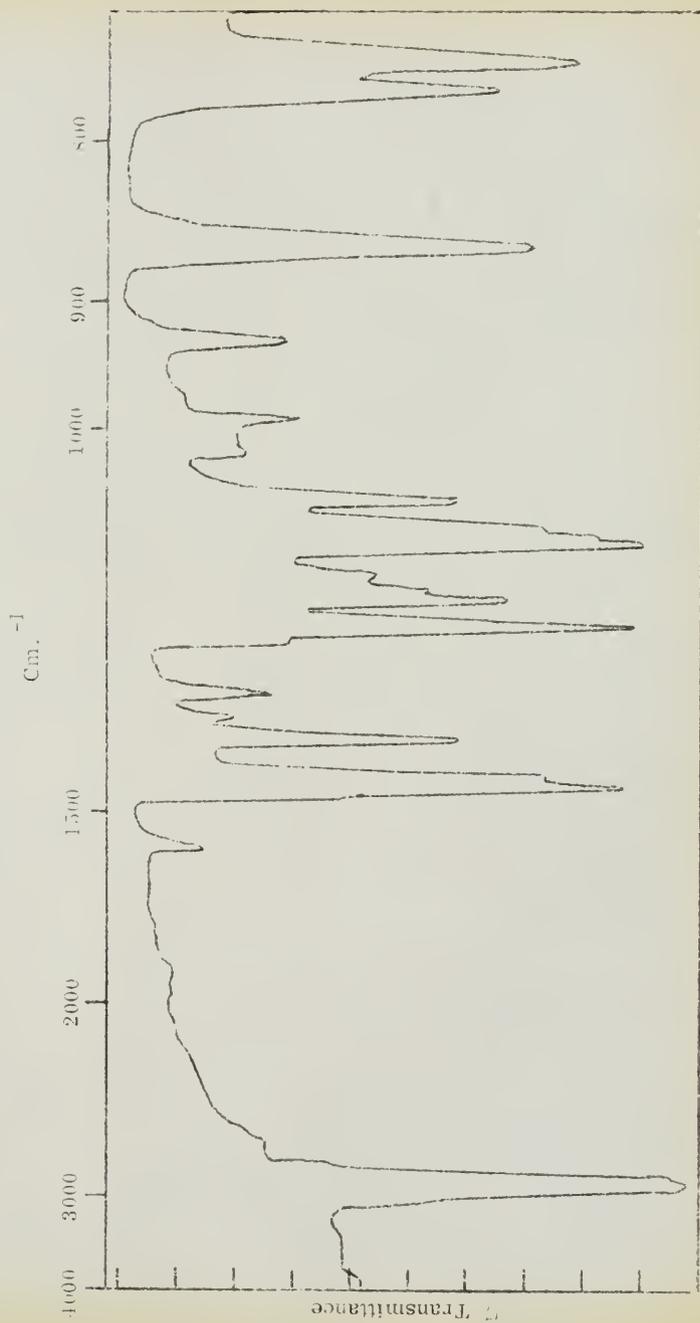


Figure 20. Infrared Spectrum of 1-Ethyl-2,2-dimethylhydrazinodipiclylphosphine Oxide (Nujol Mull).

Experiments with hydrazine and chlorodiphenylphosphines

1,2-Bis(diphenylphosphino)hydrazine. In an attempt to prepare tetrakis(diphenylphosphino)hydrazine, $[(C_6H_5)_2P]_2N-N[P(C_6H_5)_2]_2$, 1,2-bis(diphenylphosphino)hydrazine was isolated instead:



One and eight hundredths g. (0.0337 mole) anhydrous hydrazine (97 per cent) was added slowly to a solution of 29.73 g. (0.1348 mole) chlorodiphenylphosphine and 18.2 g. (0.1796 mole) triethylamine in 150 ml. chloroform. A deep yellow color developed immediately, but no precipitate formed. Heating the mixture to 65°C. for one hour had no apparent effect.

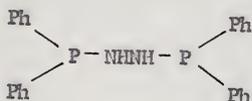
The solution was evaporated at room temperature under reduced pressure to give a white solid, which was immediately extracted with 300 ml. dry benzene and filtered to give 16.64 g. (86 per cent of theory) of triethylammonium chloride, m.p. 251-253°C.

The filtrate was evaporated to a thick paste and upon adding 300 ml. dry ether a white solid precipitated. This solid was recrystallized from acetone to give 3.60 g. (26.7 per cent of theory, based on the above equation) of a white, crystalline solid, m.p. 129.0-129.5°C.

Analysis. Found: C, 72.02; H, 5.57; P, 15.06. Calcd. for $C_{24}H_{22}N_2P_2$: C, 71.97; H, 5.54; P, 15.48.

Inasmuch as this product was recrystallized from acetone, it is unlikely that it contains the $-NH_2$ group since a hydrazine which contains the $-NH_2$ group will react with acetone to produce a hydrazone

with an entirely different elemental analysis from that given above, thus the correct structure is probably that given below:



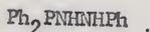
The infrared spectrum (Figure 21) is in good agreement with this structure, except that the N-H stretching absorption is not observed in its normal position, 3500-3200 cm.^{-1} , which may indicate some interaction of the phosphorus atoms with the N-H protons.

In view of the high yield of triethylammonium chloride and low yield of 1,2-bis(diphenylphosphino)hydrazine, it is possible that other, unobserved products may exist in the crude product. This system warrants further investigation.

Experiments with phenylhydrazine and chlorodiphenylphosphine

Phenylhydrazinodiphenylphosphine. Twenty-two g. (0.10 mole) chlorodiphenylphosphine in 75 ml. dry benzene was added to 21.6 g. (0.20 mole) phenylhydrazine in 75 ml. benzene. The addition was performed slowly to allow the heat to dissipate and the mixture was stirred at room temperature for one hour after addition was complete.

Upon filtration 14.5 g. (100 per cent of theory) of phenylhydrazinium chloride, m.p. 238°C. (literature value, m.p. 240°C. (70)) was obtained. Evaporation of the benzene from the filtrate left an oily liquid from which no crystals were obtained. The infrared spectrum of the liquid is consistent with the structural formula



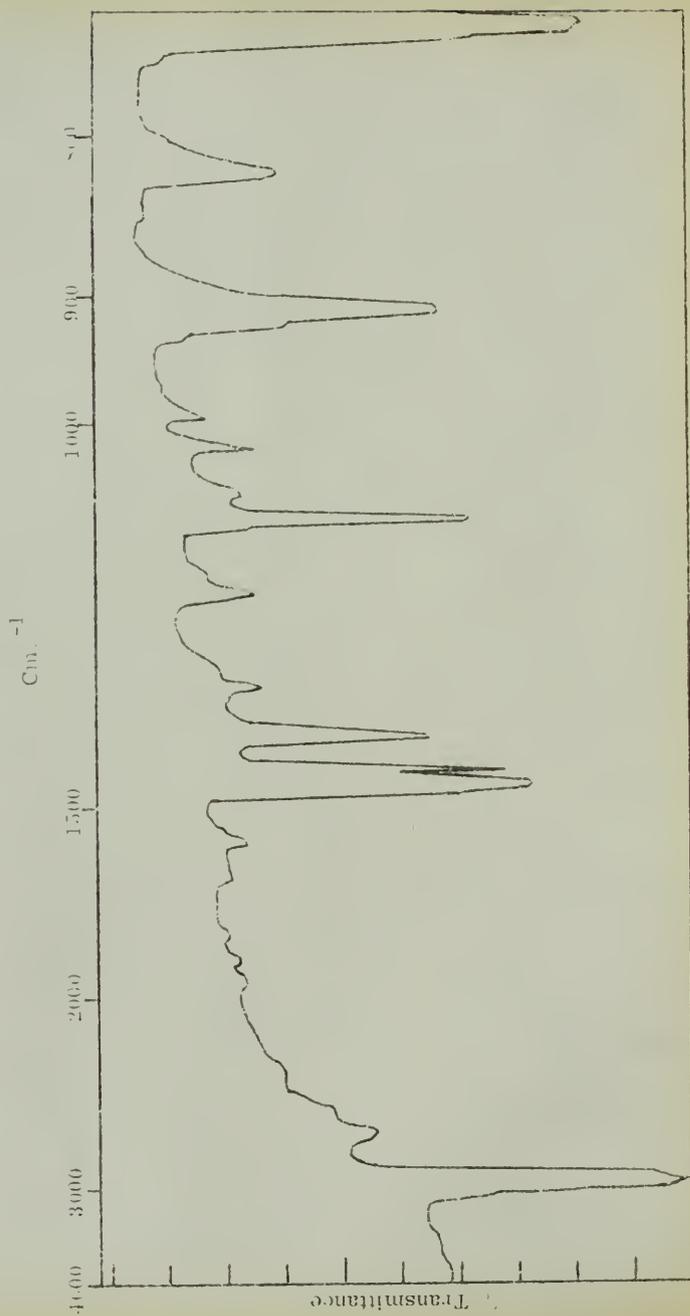


Figure 21. Infrared Spectrum of 1,2-Bis(diphenylphosphino)hydrazine (Nujol Mull)

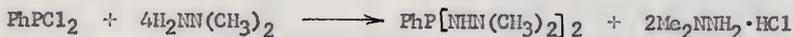
Vacuum distillation of the liquid resulted in thermal decomposition, giving a volatile fraction, b.p. 73-74°C./0.5 mm., and 17.5 g. of a resinous solid, m.p. 79-82°C. Extrapolation to the normal boiling point of the volatile fraction on a vapor pressure-temperature nomograph gives ca 135°C./760 mm. Aniline has a b.p. 184.5°C., and it is a possible product of the reaction given below:



The material balance is in accord with this suggestion, however, the solid residue is apparently a mixture of condensed species in which some oxidation has occurred, as evidenced by infrared absorption at 1175 cm^{-1} , which is characteristic of the P=O bond. The absorption frequency characteristic for the N-N bond is not present in the infrared spectrum of this material, however, it is frequently difficult to find. A weak absorption at 1250 cm^{-1} is evident, and is a characteristic absorption of the N-P=N group in phosphonitrilics.

Experiments with dichlorophenylphosphine

Bis(2,2-dimethylhydrazino)phenylphosphine.



Thirteen and fifteen hundredths g. (0.0735 mole) dichlorophenylphosphine (redistilled) in 20 ml. dry benzene was added to 23 g. (0.334 mole) 1,1-dimethylhydrazine in 25 ml. benzene. The reaction was exothermic and was therefore cooled with an external ice bath as precipitation of solid occurred at 0°C.

The mixture was filtered after a one hour period of stirring at room temperature to yield 15.28 g. (99.4 per cent of theory)

1,1-dimethylhydrazinium chloride, m.p. 79-82°C., and a yellow filtrate from which a yellow, viscous liquid was obtained upon removal of solvent at room temperature under reduced pressure.

The viscous liquid was dissolved in hot hexane and upon cooling a crop of white crystals formed, m.p. 58-60°C. Sublimation of this solid gave long, needlelike crystals, m.p. 61-63°C., which were very sensitive to the atmosphere and absorbed moisture rapidly. The yield on sublimation was very low, 12 per cent of theory, and the bulk of the material remained in the pot of the sublimation apparatus as an amber, resinous material, which pulverized readily and which became tacky upon exposure to the air. Appreciable quantities of 1,1-dimethylhydrazine were recovered from the cold trap used to protect the vacuum pump in the sublimation system.

The white, crystalline solid gave the following analysis:
 Found: C, 51.79; H, 8.15; N, 22.01; P, 14.10. Calcd. for $C_{10}H_{19}N_4P$:
 C, 53.08; H, 8.46; N, 24.77; P, 13.69.

The poor agreement of the analytical results with the suggested formula is attributed to the extreme sensitivity of the product to moisture and oxygen. The infrared spectrum (Figure 22) of this material is in good agreement with the proposed structure, but indicates that oxygen (as P=O) is an impurity.



The resinous material produced during sublimation has an analysis which is in fair agreement with that expected for a polymeric material with the repeating unit shown below:

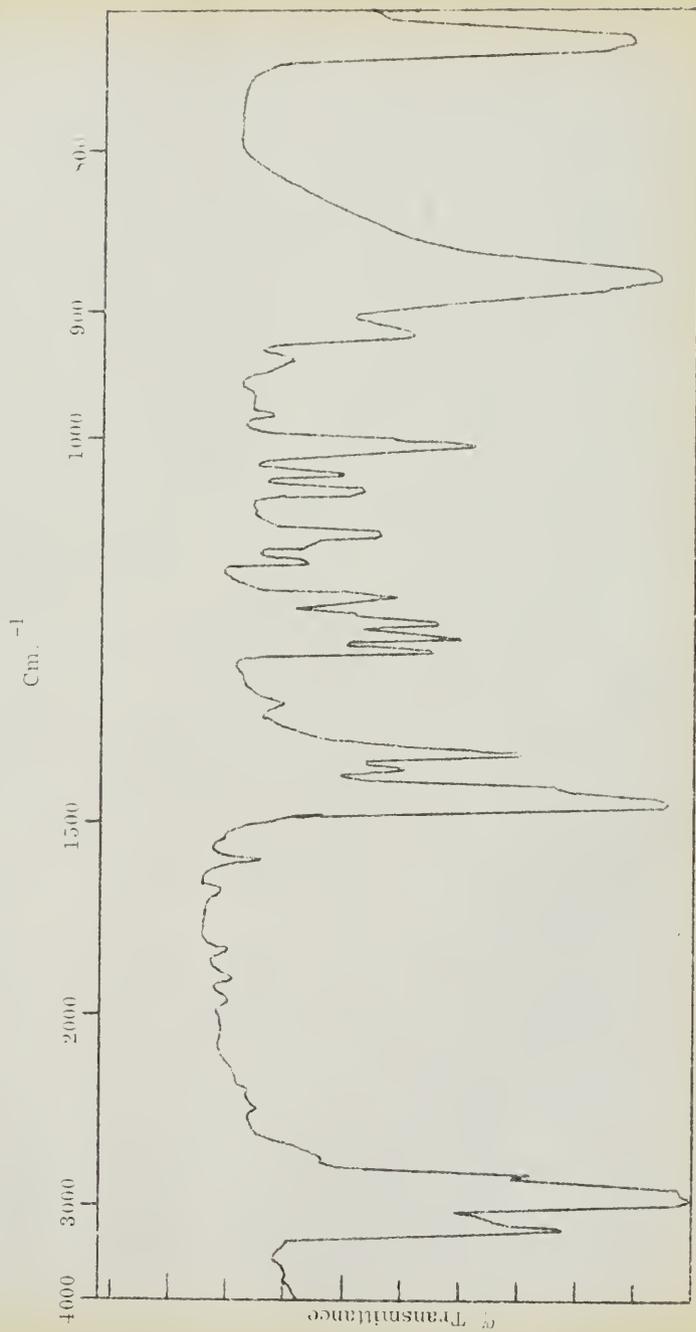
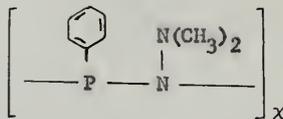


Figure 22. Infrared Spectrum of Bis(2,2-dimethylhydrazino)phenylphosphine (Nujol Mull)



Analysis. Found: C, 56.79; H, 5.54; N, 15.84; P, 21.12.

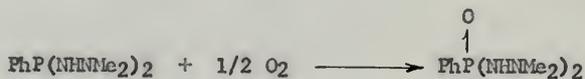
Calcd. for $\text{C}_8\text{H}_{11}\text{N}_2\text{P}$: C, 57.83; H, 6.67; N, 16.86; P, 18.64.

The molecular weight, determined cryoscopically in benzene, was 2076 for the reaction described here, which indicates an average degree of polymerization, $x = 12.5$. No attempt was made to alter the molecular weight by changing reaction conditions.

The fact that 1,1-dimethylhydrazine is produced in the thermal decomposition along with the polymer indicates that the reaction probably proceeds according to the equation below:



Oxidation of bis(2,2-dimethylhydrazino)phenylphosphine.

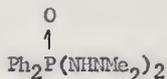


A solution of 3.6 g. bis (2,2-dimethylhydrazino)phenylphosphine in 100 ml. benzene was boiled overnight in contact with dry air. Long, needlelike crystals appeared in the solution upon cooling. These were sublimed at $160^\circ\text{C./0.20 mm.}$ gave white crystals, m.p. $161.0\text{--}163.0^\circ\text{C.}$, in 40 per cent yield, based on the equation above.

Analysis. Found: C, 49.74; H, 8.03; N, 23.01; P, 12.91.

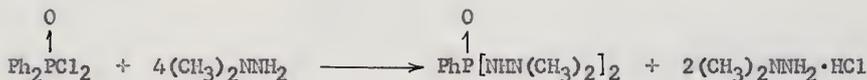
Calcd. for $\text{C}_{10}\text{H}_{13}\text{N}_4\text{PO}$: C, 49.58; H, 7.90; N, 23.13; P, 12.79.

Infrared spectral data (Figure 23) are consistent with the structural formula



This experiment serves to further characterize the product of the reaction of dichlorophenylphosphine and 1,1-dimethylhydrazine as bis(2,2-dimethylhydrazino)phenylphosphine.

Reaction of 1,1-dimethylhydrazine with phenylphosphonic dichloride.



Nineteen and five tenths g. phenylphosphonic dichloride was dissolved in 20 ml. chloroform and this was added slowly, under a nitrogen atmosphere, to a solution of 25.0 g. (0.42 mole) 1,1-dimethylhydrazine in 20 ml. chloroform. The addition took five hours; after which time the reaction mixture was warmed to 60°C., stirred for one hour, and filtered hot. The yield of 1,1-dimethylhydrazinium chloride was not quantitative; apparently this salt is somewhat soluble in chloroform.

The chloroform was evaporated at room temperature under reduced pressure to give a white solid, which was extracted twice with boiling benzene. The benzene solution deposited 17.0 g. of finely crystalline solid, m.p. 154-160°C., upon cooling. Sublimation at 160°C./0.18 mm. gave 14.5 g. (61 per cent of theory based on the equation above) of white crystals, m.p. 161.0-164.0°C.

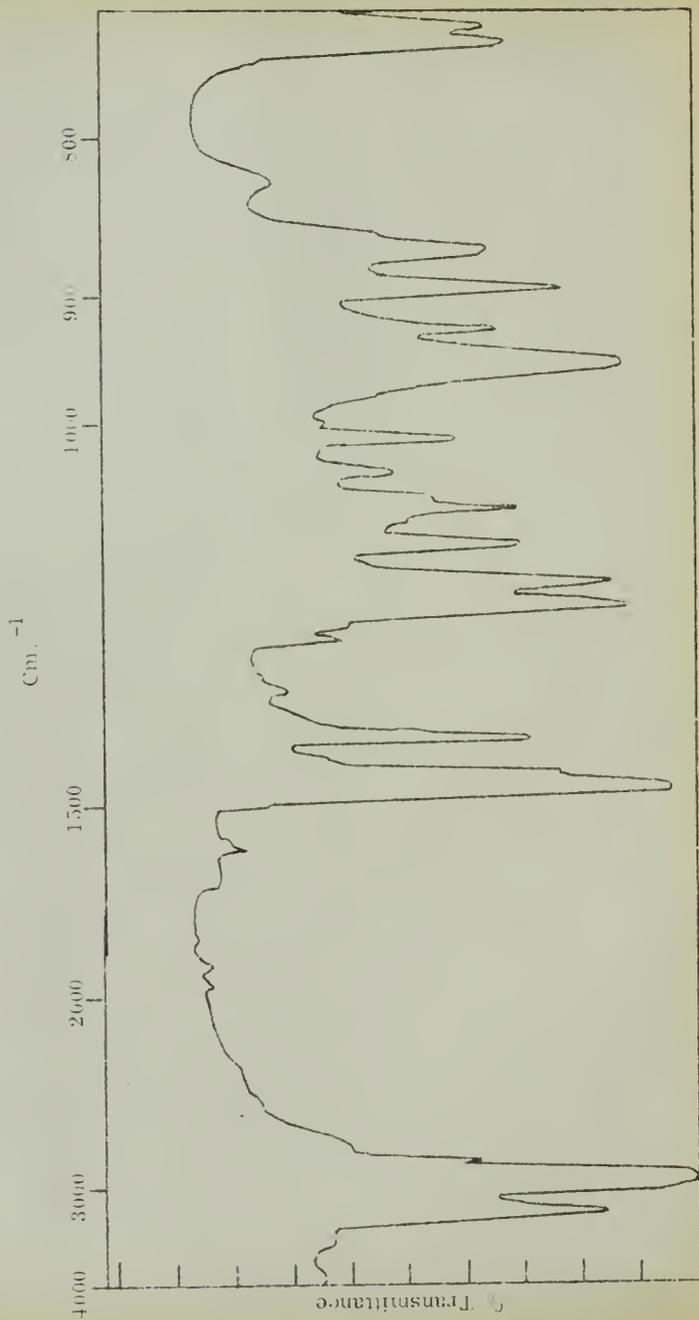
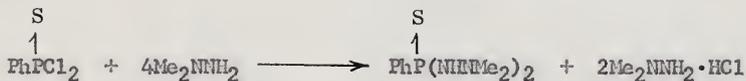


Figure 23. Infrared Spectrum of Bis(2,2-dimethylhydrazino)phenylphosphine Oxide (Nujol Mull)

A mixed melting point determination of this product with the product of the air oxidation of bis(2,2-dimethylhydrazino)phenylphosphine gave 160-162°C., and a comparison of infrared spectra of the two materials showed conclusively that they were the same compound.

This experiment serves to confirm the identity of the air oxidation product of bis(2,2-dimethylhydrazino)phenylphosphine as its oxide.

Bis(2,2-dimethylhydrazino)phenylphosphine sulfide.

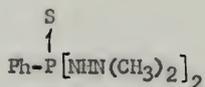


Sixteen and eighty-nine hundredths g. (0.08 mole) phenylphosphonothioic dichloride was dissolved in 25 ml. dry benzene and added to 19.6 g. (0.326 mole) 1,1-dimethylhydrazine in 25 ml. benzene. The addition was carried out at 0°C., but no evidence of reaction was observed until the reaction mixture was warmed to 10°C., at which point precipitation began. The mixture was warmed to 25°C. and stirred for one hour and then filtered to yield 14.70 g. (94.3 per cent of theory) 1,1-dimethylhydrazinium chloride.

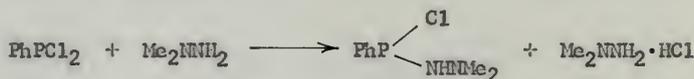
Removal of the solvent from the filtrate gave 20.10 g. of a white solid, m.p. 91-102°C. This material was recrystallized from 50 ml. of 1:1 benzene:n-hexane to give 12.8 g. of white, crystalline solid. Sublimation gave a product which melted at 106.0-106.5°C.

Analysis. Found: C, 46.43; H, 7.59; N, 21.80; P, 12.07; S, 12.25. Calcd. for C₁₀H₁₉N₄PS: C, 46.50; H, 7.41; N, 21.69; P, 11.99; S, 12.41.

The infrared (Figure 24) and n.m.r. spectra are consistent with the structural formula below.



Partial hydrazinolysis of dichlorophenylphosphine.



Seventeen and nine tenths g. (0.1 mole) dichlorophenylphosphine in 20 ml. dry benzene was added to a solution of 12.0 g. (0.20 mole) 1,1-dimethylhydrazine in 20 ml. benzene. The reaction was exothermic and required cooling. When addition was complete the mixture was stirred at room temperature for one hour and filtered to yield 9.2 g. (95 per cent of theory, based on the above equation) of 1,1-dimethylhydrazinium chloride, m.p. 79-83^o C.

Removal of the solvent at room temperature and reduced pressure gave the product: a clear, viscous liquid. The cold trap in which the solvent condensed did not contain 1,1-dimethylhydrazine, as shown by testing an aqueous extract of the solvent with KMnO_4 .

An attempt to distill the product resulted in evolution of hydrogen chloride and gave an amber, resinous material. Inasmuch as little was found useful in the way of purification, this product was not characterized other than obtaining a chlorine analysis.

Analysis. Found: Cl, 24.97. Calcd. for $\text{C}_8\text{H}_{12}\text{N}_2\text{PCl}$: 24.70.

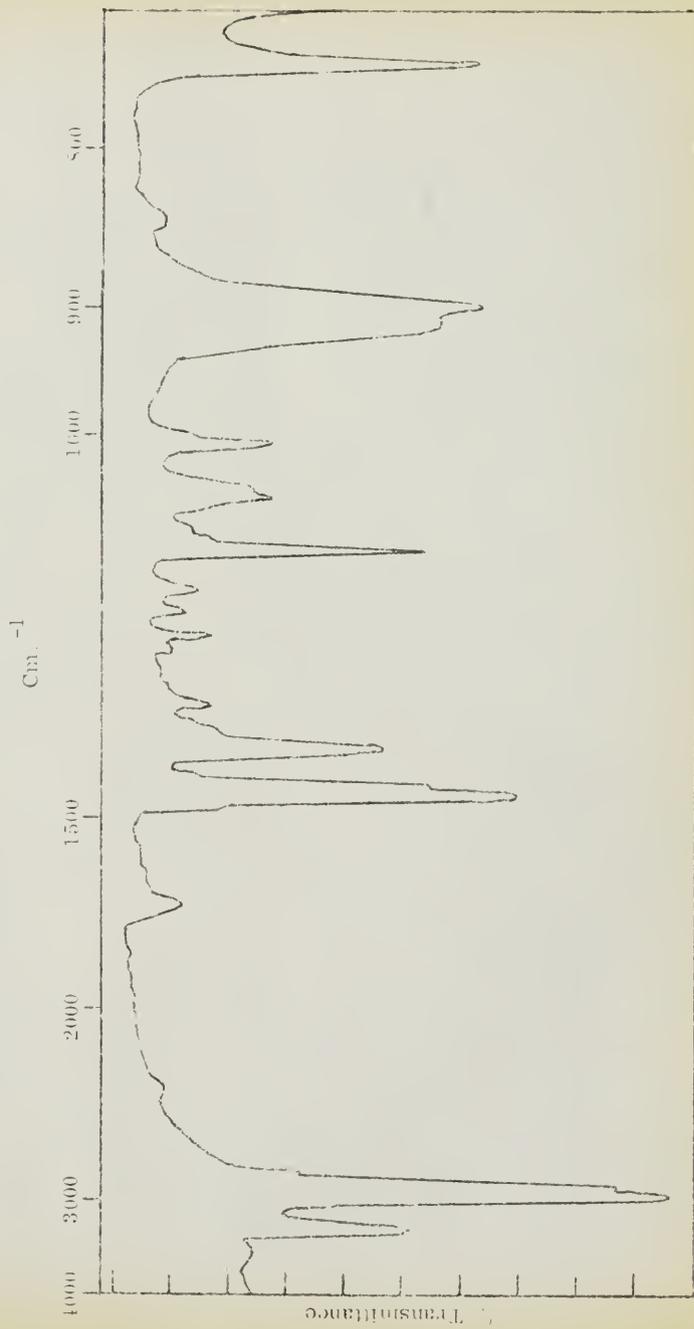


Figure 24. Infrared Spectrum of Bis(2,2-dimethylhydrazino)phenylphosphine Sulfide (Nujol Mull)

This material is extremely sensitive to oxygen and moisture and fumes in moist air.

Experiments with phosphorus trichloride

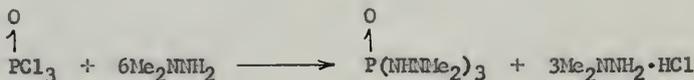
Phosphorus tri(2,2-dimethylhydrazide).



Six and eighty-seven hundredths g. (0.05 mole) phosphorus trichloride in 25 ml. dry benzene was added slowly, under a nitrogen atmosphere, to 24.06 g. (0.4 mole) 1,1-dimethylhydrazine at 0°C. Precipitation began as the solution was warmed to room temperature and continued as the solution was warmed to 35°C. The mixture was stirred at 30°C. for one hour and filtered to give 13.8 g. (95 per cent of theory) 1,1-dimethylhydrazinium chloride.

Upon removal of the solvent from the filtrate the product was obtained as a yellow, viscous liquid, which contained no chlorine, as determined by testing a small aqueous extract with silver nitrate solution. The product could not be distilled and thus no characterization was attempted; rapid reaction with moist air was noted, however, and an exposed sample quickly absorbs moisture from the air and becomes tacky.

Phosphoryl tri(2,2-dimethylhydrazide).



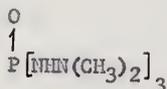
Eight and twenty-one hundredths g. (0.0535 mole) phosphoryl chloride in 25 ml. chloroform was added over a two hour period to 20.0 g.

(0.33 mole) 1,1-dimethylhydrazine in 25 ml. chloroform at 0°C. The temperature was raised to 30°C. and stirred for one hour and filtered to give 9.97 g. (64 per cent of theory, based on the above equation) 1,1-dimethylhydrazinium chloride.

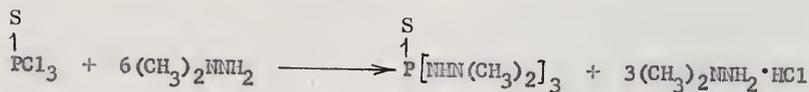
The filtrate was evaporated at room temperature under reduced pressure and then extracted with hot benzene and filtered. Upon cooling, the benzene solution deposited a white crystalline solid which was then sublimed at 105°C./0.10 mm. to give 3.79 g. (76 per cent of theory) of white, crystalline product which melted at 193.5-194.0°C.

Analysis. Found: C, 31.67; H, 9.57; N, 37.03; P, 13.56.
Calcd. for $C_6H_{21}N_6PO$: C, 32.14; H, 9.44; N, 37.48; P, 13.81.

The infrared (Figure 25) and n.m.r. spectra are consistent with the structural formula given below.



Thiophosphoryl tri(2,2-dimethylhydrazide).



Thirty-seven g. (0.62 mole) 1,1-dimethylhydrazine was dissolved in 20 ml. dry benzene and to this was added with stirring and cooling a solution of 10.64 g. (0.063 mole) thiophosphoryl chloride in 20 ml. benzene. When addition was complete the mixture was warmed to 45°C. and stirred for 30 minutes and filtered.

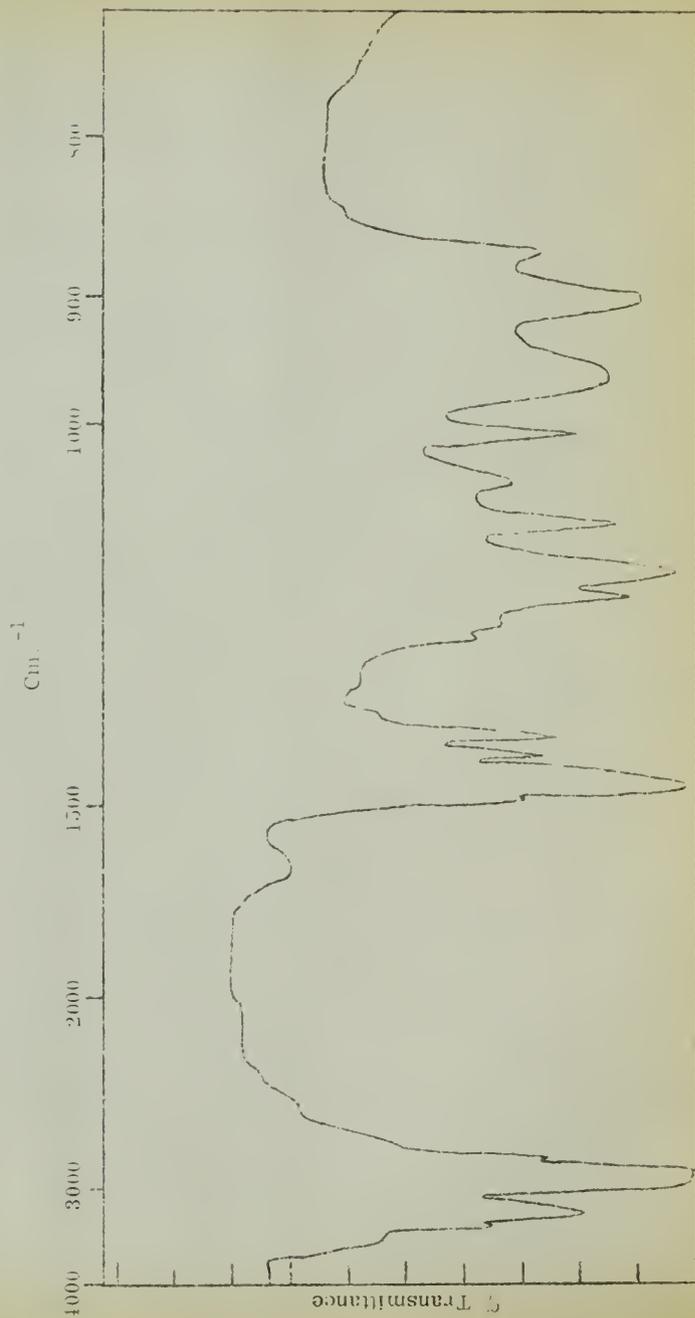


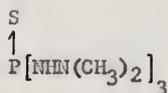
Figure 25. Infrared Spectrum of Phosphoryl Tri(2,2-dimethylhydrazide). (Nujol Mull)

Eighteen and six tenths g. 1,1-dimethylhydrazinium chloride was collected on the filter, and 15.0 g. (99 per cent of theory) white solid was obtained upon evaporation of the solvent at room temperature and reduced pressure.

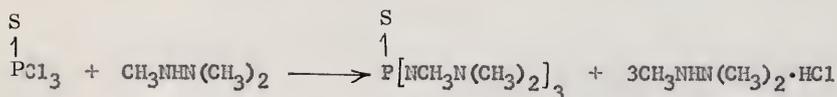
Sublimation of the crude product gave 7.5 g. (50 per cent yield) white, crystalline solid, m.p. 75.5-78.0°C.

Analysis. Found: C, 29.74; H, 8.52; N, 35.07; P, 13.07; S, 13.49. Calcd. for $C_6H_{21}N_6PS$: C, 29.99; H, 8.81; N, 34.97; P, 12.89; S, 13.34.

The infrared (Figure 26) and n.m.r. spectra are consistent with this structure:



Thiophosphoryl tri(1,2,2-trimethylhydrazide).



Five and eight hundredths g. (0.03 mole) thiophosphoryl chloride was reacted with 14.83 g. (0.20 mole) 1,1,2-trimethylhydrazine in 50 ml. benzene at 0-5°C., under a nitrogen atmosphere. The solution was warmed to room temperature after addition and the precipitated salt was filtered from the mixture. Nine and eighty hundredths g. 1,1,2-trimethylhydrazinium chloride, m.p. 54-56°C., was collected on the filter (98.6 per cent yield).

Upon evaporation of the solvent at room temperature and reduced pressure there was obtained a yellow gum. Crystallization was

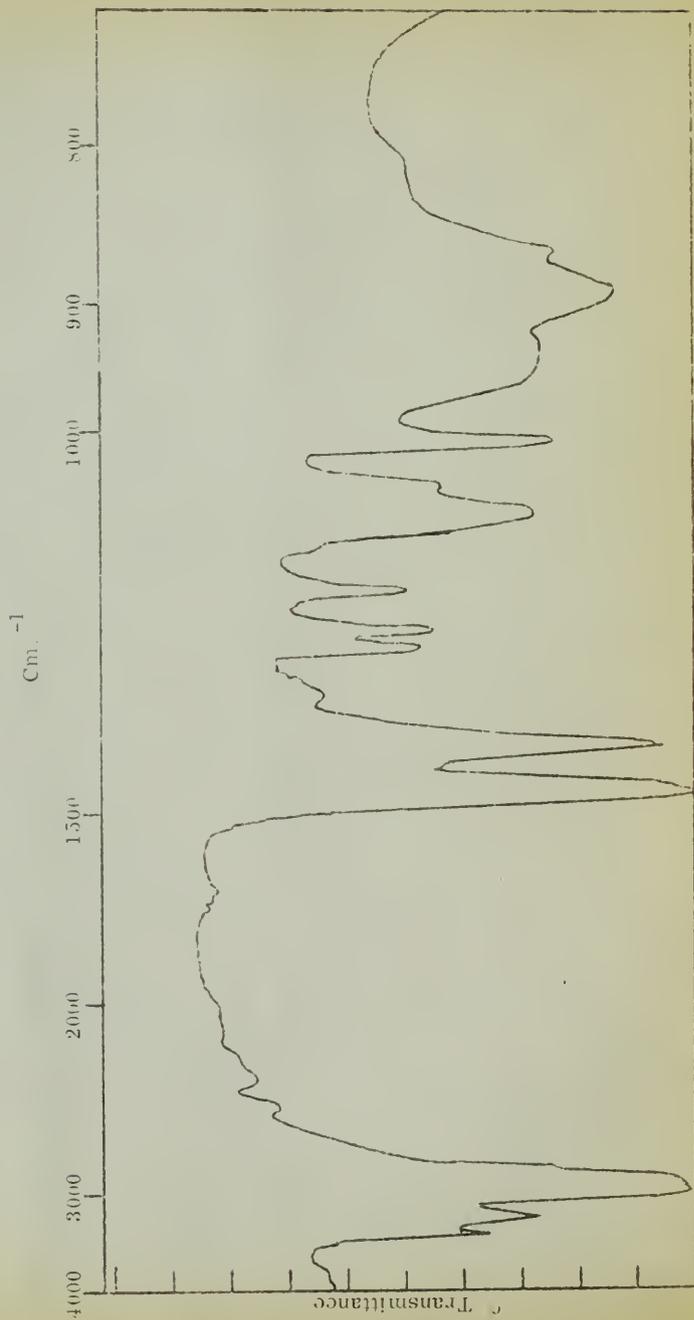


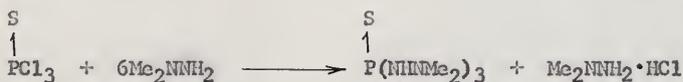
Figure 26. Infrared Spectrum of Thiophosphoryl Tri(2,2-dimethylhydrazide). (Nujol Mull)

attempted by cooling the gum, but neither this treatment nor the addition of cyclohexane or ether caused formation of solid product.

Rapid decomposition occurred when an attempt was made to purify the product by vacuum distillation. The decomposition temperature was 165°C./0.4 mm.

No further characterization was attempted.

Thiophosphoryl tri(1-ethyl-2,2-dimethylhydrazide).



Four g. (0.0236 mole) thiophosphoryl chloride was dissolved in 25 ml. dry benzene and added to 13.2 g. (0.15 mole) 1-ethyl-2,2-dimethylhydrazine over a one hour period at 0°C. The mixture was then warmed to 30°C. and stirred for one hour and filtered to give 5.5 g. (62 per cent of theory) 1-ethyl-2,2-dimethylhydrazinium chloride, m.p. 56-57°C. An additional lot of 1-ethyl-2,2-dimethylhydrazinium chloride was obtained by stirring the filtrate for 15 hours at 30°C. The melting point of this lot was 57-60°C., and from infrared spectral data it was determined that the salt was contaminated with a phosphorus-containing compound.

Successive lots of precipitate, obtained by allowing the solvent to evaporate slowly, had higher melting points and the intensity of the infrared absorption frequency associated with the P-S bond at 722 cm.⁻¹ increased in intensity.

A number of solvents were tried in order to find one which will separate the desired product from 1-ethyl-2,2-dimethylhydrazinium

chloride, but apparently this salt is soluble in the solvents one would expect to dissolve thiophosphoryl tri(2,2-dimethylhydrazide), thus no separation was made.

An alternate route to the synthesis of this compound would be to use a tertiary amine as an hydrogen chloride acceptor so that the salt formed would not be soluble in benzene or chloroform. This method is still untried in this particular system.

Discussion

Infrared analysis

An infrared spectrum was obtained on each hydrazinophosphine and derivative prepared in the course of this work and the absorption frequencies found in the more significant compounds were tabulated (Table 26). Assignments are found in Table 27. Most of the spectra were obtained from Nujol mulls since most of the compounds studied are crystalline solids; diphenylphosphine is an exception and its spectrum was obtained in a 0.0295 mm. cell without solvent.

The assignments made are on the basis of known absorption frequencies (71,72) and by comparison of the various spectra in which a frequency is observed which can be correlated with a particular group. The infrared spectra are in excellent agreement with those expected on the basis of the anticipated molecular structures.

No unusual shifts in the absorption frequencies are observed except in the case of the N-N absorption band which is usually found in the vicinity of 950 cm.^{-1} and which is often very weak and difficult

14

700
M

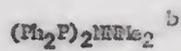
692
S



14

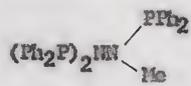
704
M

695
S



711
S

693
S



14

693
S



TABLE 26

Principal Infrared Absorption Frequencies for Some Phosphorus Hydrasine Derivatives^a

$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b	3273	3030	2780	2650		1920	1830	1800	1565	1440	1442	1430	1373	1266	1222	1211	1157	1090	1064	1062	1036	1005	998	880	746	730	700	693	$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b													
$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b	3090	2950	2900			1940	1880	1800	1587	1467	1445	1430	1300	1310	1216	1160	1155	1120	1091	1070	1030	1000	991	908	843	730	726	720	704	690	$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b											
$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b	3030	2945	2870			1950	1880	1805	1573		1453	1430	1370	1300		1176	1155	1110	1087	1062		993	938	918	886		746	740	711	693	$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b											
$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b	3030	2990	2900	2616		1950	1870	1800	1560	1460	1460	1430	1374	1379		1175	1150		1090	1069		1025	1000	996	920	909	813	710	745	724	693	$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b										
$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b	3030	3000	3000	2900	2800	1890	1951	1875	1800	1430	1545	1460	1460	1460	1378	1300		1230	1217	1165	1160		1062	1000	1000	1035	1016	1009	980	945	874	915	875	697	686	$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b						
$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b	3450		3100	2980	2670	2715			1957	1900	1813		1540		1460	1440	1405	1372		1225	1200	1183	1160	1134	1107	1072	1042		1025	1010	956	927	917	859		693	$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b					
$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b	3270	3080	2920	2900			1900	1850	1790		1570	1530	1460	1465	1440	1400	1378	1358	1316		1230	1202	1190	1160	1109		1070	1040		1025	1018	978	944	850	825	710	747	713	697	$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b		
$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b	3090	3000	2950	2660			1973	1901	1800		1567		1458	1440		1378	1309	1240	1230		1175	1150	1130	1100	1075		1025	1000	900	928	898	848	830		738	722	709	705	694	$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b		
$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b	3080	2950	2880	2715					1573		1452	1437		1374	1227	1300		1283	1209	1176	1145	1118	1093	1042			1025	991	983	929	902	862		773	759		722	703	694	$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b		
$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b	3090	2945	2680				1960	1900	1810		1573	1473	1451	1437	1430	1373	1305		1227	1210	1181	1141		1100	1064		1016	998	998		860		773	753	732		715	694	674	$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b		
$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b	3450	3100	2900	2805			1960	1900	1820		1376		1456	1432		1380	1205		1230	1212	1181	1141		1078	1072	1045		1018	920	923	896	838	827		730	745	718		697	$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b		
$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b	3430	3020	2910	2900	2600	1700				1460	1441		1378	1308		1227	1220	1173	1140	1127			1060	1030			1010		915	900	843		757		723		700	$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b				
$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b	3030	3000	2900	2800		1483				1460	1460		1400	1376		1300		1237	1213		1130		1091		1055			1010	900		902	869				720		$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b				
$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b	3400	3100	3160	3000	2900	2800				1465	1460		1390	1360		1293		1230	1210		1180		1092	1076	1030			1012	960		890	867	833				728		$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b			
$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b	3400	3100	2990	2915		2300	1930	1880	1800		1578	1478	1458	1438		1370	1318	1293			1150	1120			1042			1007	943		928	897	888	849	823	773		718	693	686	$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b	
$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b	3030	2940	2700				1960	1860	1800		1565	1480	1470	1440	1430	1360	1318	1290			1184	1157		1100	1072	1040		1016		988		907		821		747	745	717	711	690	$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b	
$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b	3030		2900	2830	2280		1900	1865	1800		1580	1473		1430	1370	1323	1300	1260			1173	1152		1091	1045			1025	1000		915	880	840	802			742	730	705	693	671	$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b
$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b		2945	2900								1460				1360																							722		$(\text{H}_2\text{N})_2\text{P}(\text{NH}_2)_2$ ^b		

^acm⁻¹. ^bliquid cell. ^ccalc. plot.

TABLE 27

Infrared Absorption Frequencies and Assignments

Group	Range (Cm. ⁻¹)
N-H (free)	3450-3590 (w)
N-H (associated)	3175-3320 (w-m)
C-H (stretch, aromatic)	3030-3100 (s)
C-H (stretch, aliphatic)	2880-3000 (s), 2610-2800 (w-m)
P-H	2280 (m)
phenyl, mono-substituted	1900-1975 1835-1900 (w-triplet) 1790-1880
N-H (deformation)	1625-1700 (w)
phenyl, skeletal in-plane vibrations	1565-1590 (w)
C-H (deformation, aromatic)	1475-1487 (w-m)
C-H (deformation, aliphatic)	1451-1470 (m) 1370-1380 (w) (doublet)
P-phenyl	1430-1440 (s)
-NR ₂ , N-CH ₃	1390-1430 (w-m)
C-CH ₃	1373-1380 (w-m)
phenyl	1318-1358 (w)
P=O	1175-1188 (m-s)
phenyl (near P=O or P=S), mono-substituted	1109-1220 (m-s)
N-CH ₃	1040-1050 (w-m)
N-N	950-996 (w)
N-H	880-917 (m-s)
P-N	743-773 (m-s)
C-H chains, P=S	700-727 (m-s)
phenyl (C-H, out-of-plane deformations)	690-697 (m-s), 671-688 (m)

to locate. In most hydrazinophosphorus compounds, as in alkyl hydrazines, the N-H absorption frequency is found in the range, 943-960 cm.^{-1} . In some of the hydrazinophosphorus compounds, the absorption is weak and difficult to find.

The various N-H absorption frequencies are observed in the spectra of those hydrazinophosphorus compounds which are expected to contain the N-H bond, and a new, intense band in the range 880-917 cm.^{-1} is observed in all the N-H containing hydrazinophosphorus compounds, but not in the trialkylhydrazine derivatives, which do not contain the N-H bond.

Many characteristic bands are observed which are distinct and easily located: P=O, 1175-1188 cm.^{-1} ; P-phenyl, 1430-1440 cm.^{-1} ; and P-H, 2280 cm.^{-1} . Other bands which are more difficult to find and which are frequently obscured include the N-CH₃ (1390-1430 cm.^{-1}), the P-N (743-773 cm.^{-1}), and the P=S (700-727 cm.^{-1}) bands.

The absorption frequencies associated with the C-C and C-H bonds, as well as those assigned to aromatic ring vibrations, are all found in the ranges described in the literature (71), but the monosubstituted phenyl ring band at 1109-1220 cm.^{-1} appears to be intensified by the proximity of the P=O and P=S groups. This band is not found in hydrazinophosphines, but is found in hydrazinophosphine oxides and hydrazinophosphine sulfides.

The observation that P=O and P=S groups intensify monosubstituted phenyl absorption in the infrared leads one to speculate

as to whether the absorption frequency range commonly assigned to P=O , $1175\text{-}1188\text{ cm.}^{-1}$ (71), is actually a P=O absorption or an attenuated aromatic ring vibration in diphenylphosphino- compounds which contain the P=O bond. A band in this region is observed in all diphenylphosphino- compounds, but unless the P=O group is present the peak is extremely weak, and is commonly regarded as being due to the presence of oxygen (in the form of P=O) as an impurity.

There is some question as to the actual bond order of the P-N bond in hydrazinophosphines and other compounds which contain the P-N bond. The infrared spectrum is a potential tool for solving the problem, but to date no one has collected extensive data on the P-N absorption frequencies, and it has been common practice to include a rather wide range of infrared values in the characterization of the P-N bond, $750\text{-}870\text{ cm.}^{-1}$ (72). This wide range leaves room for speculation as to the actual absorption frequency associated with a P-N single bond. In our work we have narrowed this range to $743\text{-}773\text{ cm.}^{-1}$ which seems to include all our examples.

Nuclear magnetic resonance analysis

The n.m.r. spectra of many of the hydrazinophosphorus compounds synthesized in this study were obtained and the data are tabulated in Table 28. The chemical shift is expressed in τ values for protons and in parts per million (ppm.) for the ^{31}P nucleus. The pattern and splitting observed for multiplets are given and assignments are made for the various signals found. The relative areas of the peaks are not given; however, these are all in very good agreement with the proposed structures of the compounds studied.

TABLE 28

Nuclear Magnetic Resonance Data Summary

Formula	Solvent	Frequency	Reference	Peak	Chem. Shift	Pattern/Splitting
$(Ph)_2PNH(CH_3)_2$	$CDCl_3$	56.4 mc.	C_6H_6 (ext.)	H(phenyl)	1.9 τ	complex
	$CDCl_3$	56.4 mc.	C_6H_6 (ext.)	H(N-H)	6.0 τ	doublet
	$CDCl_3$	56.4 mc.	C_6H_6 (ext.)	H(N- CH_3)	6.8 τ	singlet
$(Ph)_2P_2NN(CH_3)_2$	C_6H_6	60.0 mc.	Me_4Si (int.)	H(phenyl)	obscured	---
	C_6H_6	60.0 mc.	Me_4Si (int.)	H(N- CH_3)	7.52 τ	singlet
	C_6H_6	19.3 mc.	H_3PO_4 (subs.)	P	-47.4 ppm.	broad
$Ph_2PNH(CH_3)_2$	$CDCl_3$	60.0 mc.	Me_4Si (int.)	H(phenyl, ortho H)	2.07 τ	---
	$CDCl_3$	60.0 mc.	Me_4Si (int.)	H(phenyl, meta, para H)	2.55 τ	---
	$CDCl_3$	60.0 mc.	Me_4Si (int.)	H(N-H)	5.53 τ	doublet (18.8 cps.)
$Ph_2PNH(CH_3)_2$	$CDCl_3$	60.0 mc.	Me_4Si (int.)	H(N- CH_3)	7.42 τ	singlet
	$CDCl_3$	19.3 mc.	H_3PO_4 (subs.)	P	-22.0 ppm.	broad

TABLE 28 Continued

Formula	Solvent	Frequency	Reference	Peak	Chem. Shift	Pattern/Splitting
$\text{Ph}_2\text{PNHN}(\text{CH}_3)_2$	CDCl_3	60.0 mc.	Me_4Si (int.)	H(phenyl, ortho H)	1.97 τ <u>au</u>	---
	CDCl_3	60.0 mc.	Me_4Si (int.)	H(phenyl, meta, para H)	2.66 τ <u>au</u>	---
	CDCl_3	60.0 mc.	Me_4Si (int.)	H(N-H)	6.21 τ <u>au</u>	doublet (21.5 cps.)
	CDCl_3	60.0 mc.	Me_4Si (int.)	N(N- CH_3)	7.61 τ <u>au</u>	singlet
	CDCl_3	19.3 mc.	H_3PO_4 (subs.)	P	-57.3 ppm.	broad
	CDCl_3	60.0 mc.	Me_4Si (int.)	H(phenyl, ortho H)	2.12 τ <u>au</u>	---
	CDCl_3	60.0 mc.	Me_4Si (int.)	H(phenyl, meta, para H)	2.61 τ <u>au</u>	---
	CDCl_3	60.0 mc.	Me_4Si (int.)	H(N- CH_3)	7.45 τ <u>au</u>	doublet (10.5 cps.)
	CDCl_3	60.0 mc.	Me_4Si (int.)	H N(CH_3)	7.61 τ <u>au</u>	singlet
	CDCl_3	19.3 mc.	H_3PO_4 (subs.)	P	-23.2 ppm.	broad

S

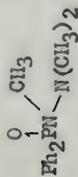


TABLE 28 Continued

Formula	Solvent	Frequency	Reference	Peak	Chem. Shift	Pattern/Splitting
$\begin{array}{c} \text{O} \\ \\ \text{Ph}_2\text{PN} \\ \\ \text{CH}_2\text{CH}_3 \\ \\ \text{N}(\text{CH}_3)_2 \end{array}$	CDCl ₃	60.0 mc.	Me ₄ Si (int.)	H(phenyl, ortho H)	2.06 τ	---
	CDCl ₃	60.0 mc.	Me ₄ Si (int.)	H(phenyl, meta, para H)	2.54 τ	---
	CDCl ₃	60.0 mc.	Me ₄ Si (int.)	H(-CH ₂ -)	6.75 τ	quadruplet (7.1 cps.) doublet (ca. 7 cps.)
	CDCl ₃	60.0 mc.	Me ₄ Si (int.)	H(N-CH ₃)	7.48 τ	singlet
	CDCl ₃	60.0 mc.	Me ₄ Si (int.)	H(CH ₃ -CH ₂ -)	8.83 τ	triplet (6.9 cps.)
	CDCl ₃	19.3 mc.	H ₃ PO ₄ (subs.)	P	-26.2 ppm.	broad
	CDCl ₃	60.0 mc.	CH ₃ CHO (subs.)	H(phenyl, ortho H)	1.82 τ	---
	CDCl ₃	60.0 mc.	CH ₃ CHO (subs.)	H(phenyl, meta, para H)	2.46 τ	---
$\begin{array}{c} \text{S} \\ \\ \text{Ph}_2\text{PN} \\ \\ \text{CH}_2\text{CH}_3 \\ \\ \text{N}(\text{CH}_3)_2 \end{array}$	CDCl ₃	60.0 mc.	CH ₃ CHO (subs.)	H(-CH ₂ -)	6.67 τ	quadruplet (7 cps.) doublet (3 cps.)

TABLE 28 Continued

Formula	Solvent	Frequency	Reference	Peak	Chem. Shift	Pattern/Splitting	
$\text{Ph}_2\text{P}^1[\text{N}(\text{CH}_3)_2]_2^2$	CDCl_3	60.0 mc.	CH_3CHO (subs.)	H(N- CH_3)	7.48 τ	singlet	
	CDCl_3	60.0 mc.	CH_3CHO (subs.)	H($\text{CH}_3\text{-CH}_2\text{-}$)	3.76 τ	triplet (7 cps.)	
	CDCl_3	19.3 mc.	H_3PO_4 (subs.)	P	-66.4 ppm.	broad	
	CDCl_3	60.0 mc.	Me_4Si (int.)	H(phenyl, ortho H)	1.84 τ	---	
	CDCl_3	60.0 mc.	Me_4Si (int.)	H(phenyl, meta, para H)	2.56 τ	---	
	CDCl_3	60.0 mc.	Me_4Si (int.)	H(N-H)	6.33 τ	doublet (27.3 cps.)	
	CDCl_3	60.0 mc.	Me_4Si (int.)	H(N- CH_3)	7.51 τ	singlet	
	CDCl_3	19.3 mc.	H_3PO_4 (subs.)	P	-61.1 ppm.	broad, perhaps a septuplet (12 cps.)	
	$\text{P}^0[\text{N}(\text{CH}_3)_2]_3^1$	CDCl_3	60.0 mc.	Me_4Si (int.)	H(N-H)	6.05 τ	doublet (23.7 cps.)
		CDCl_3	60.0 mc.	Me_4Si (int.)	H(N- CH_3)	7.43 τ	singlet
CDCl_3		19.3 mc.	H_3PO_4 (subs.)	P	-12.5 ppm.	quadruplet (23 cps.)	

The information sought in this segment of the work, other than confirmation of the assigned structural formulae, concerns the relative electron densities around the nucleus studied, ^{31}P .

Since the chemical shift is a phenomenon directly associated with the diamagnetic shielding around the nucleus, these quantities can be correlated and it may then be said that, in general, the chemical shift is a function of the electron density around the nucleus; low chemical shift values (downfield from an arbitrary reference) are associated with low electron density, and high chemical shift values indicate high electron density around the nucleus.

The ^{31}P nucleus has a larger chemical shift than does ^1H because the presence of electrons in higher energy orbitals in the phosphorus atom allows for greater polarizability of the phosphorus atom than of the hydrogen atom.

Table 29 shows a scale of the chemical shift values observed for some hydrazinophosphorus compounds. This scale shows that, among the compounds considered, the electron density about the phosphorus atom is greatest for hydrazinophosphine oxides and least for hydrazinophosphine sulfides.

Although it would be desirable to have additional information upon which to base generalizations, an adequate argument for rationalizing the positions of these compounds on the scale can be made.

The stereochemistry of a phosphine oxide or sulfide may be described as a distorted tetrahedral structure such as that indicated below.

TABLE 29

Scale of Chemical Shift Values from N.M.R. Data

Chemical Shift (ppm.)	Compound
-12.5	$\begin{array}{c} \text{O} \\ \\ \text{P}(\text{NHNMe}_2)_3 \end{array}$
-22.0	$\begin{array}{c} \text{O} \\ \\ \text{Ph}_2\text{P}(\text{NHNMe}_2) \end{array}$
-26.2	$\begin{array}{c} \text{O} \\ \\ \text{Ph}_2\text{P}(\text{NEtNMe}_2) \end{array}$
-28.2	$\begin{array}{c} \text{O} \\ \\ \text{Ph}_2\text{P}(\text{NMeNMe}_2) \end{array}$
-47.4	$(\text{Ph}_2\text{P})_2\text{NMe}_2$
-57.3	$\begin{array}{c} \text{S} \\ \\ \text{Ph}_2\text{P}(\text{NHNMe}_2) \end{array}$
-61.1	$\begin{array}{c} \text{S} \\ \\ \text{PhP}(\text{NHDMe}_2)_2 \end{array}$
-64.4	$\begin{array}{c} \text{S} \\ \\ \text{Ph}_2\text{P}(\text{NEtNMe}_2) \end{array}$



In the oxide, back-donation of electrons from the oxygen atom to the phosphorus atom can occur in $p\pi$ - $d\pi$ bonding, thus delocalizing a portion of the electron density about the oxygen atom towards the phosphorus atom. In the sulfide, such back-donation is unlikely because of the larger internuclear distance between the phosphorus and sulfur atoms and the fact that higher energy orbitals would have to be used by the sulfur than are favorable for such back-donation. The electron density about the phosphorus atom is thus greater in phosphine oxides than it is in phosphine sulfides.

The same effect, back-donation of electron charge, is responsible for the lower reactivity of phosphine oxides compared with phosphine sulfides and unoxidized phosphines since those chemical reactions which depend on nucleophilic attack of a basic species on the phosphorus atom are favored by the phosphorus atom which has least electron density about it and which has available vacant d -orbitals for such attack.

Interpretation of synthetic results

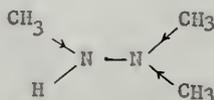
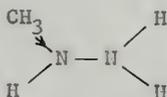
Hydrazinolysis of the phosphorus-chlorine bond. It has been amply demonstrated by the synthetic results reported in this study that hydrazinolysis of the phosphorus-chlorine bond is a general reaction and may be applied to mono-, di-, and trichlorophosphorus compounds, with phosphorus in the three-covalent or four-covalent state.

Observations of the reaction conditions show that different chlorophosphorus compounds and hydrazines vary in reactivity. The temperature of a reaction mixture containing a hydrazine and a chlorophosphorus compound does not rise appreciably until the hydrochloride salt of the hydrazine (or tertiary amine) begins to precipitate; thus, the temperatures associated with the first appearance of precipitate are characteristic of individual reactions.

Most hydrazinolyses will occur below 25°C.; however, a few of the reactions observed required elevated temperatures. Qualitative observations of the reactions of several chlorophosphorus compounds with 1,1-dimethylhydrazine show that the reactions become increasingly exothermic in the order $\text{Ph}_2\text{P}(\text{O})\text{Cl} < \text{Ph}_2\text{PCl} < \text{PhP}(\text{S})\text{Cl}_2 < \text{P}(\text{S})\text{Cl}_3 < \text{PhP}(\text{O})\text{Cl}_2 < \text{P}(\text{O})\text{Cl}_3 < \text{PhPCl}_2 < \text{PCl}_3$.

Experiments with chlorodiphenylphosphine and various hydrazines showed that reactivity in a series of hydrazines increases in the order $\text{EtNHMe}_2 < \text{MeNHMe}_2 < \text{Me}_2\text{NHNH}_2 < \text{NH}_2\text{NH}_2$.

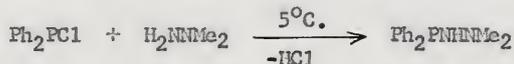
The reactivity of these hydrazines is explained by the classical inductive effect if we assume that the hydrazine participates in the reaction as a proton source, in which case the hydrazine with the most acidic protons should be most reactive. Thus, methylhydrazine is more reactive than trimethylhydrazine which is the less acidic of the two.



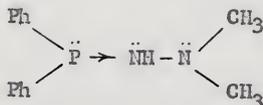
It is possible to remove all the protons from a hydrazine (except hydrazine itself) using chlorodiphenylphosphine, and removal of the first proton can be accomplished at low temperatures, seldom above 35°C. However, as the second and third proton is removed higher temperatures are required (up to 110°C.).

In an attempt to substitute all four protons on hydrazine, disubstitution and the formation of 1,2-bis(diphenylphosphino)-hydrazine, $\text{Ph}_2\text{PNNHPPh}_2$, resulted and no tetrasubstituted product was isolated.

Since the substitution of the second proton in 2,2-dimethylhydrazinodiphenylphosphine will proceed only at higher temperatures than that required for the first hydrazinolysis,



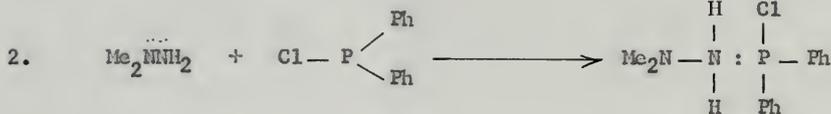
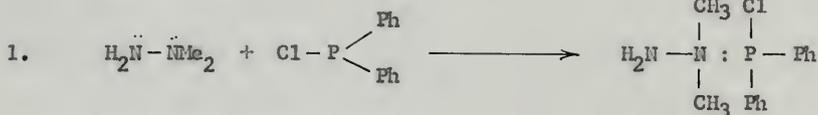
the proton in the N-H group in 2,2-dimethylhydrazinodiphenylphosphine is apparently less active than that in 1,1-dimethylhydrazine. In order to deactivate this proton it is necessary to increase the electron density about the nitrogen atom in the N-H group, which leads to the postulate that the diphenylphosphino- group is electron-donating and deactivates the second proton towards substitution.



Mechanism of hydrazinolysis. The mechanism of hydrazinolysis of chlorophosphorus compounds probably involves nucleophilic attack

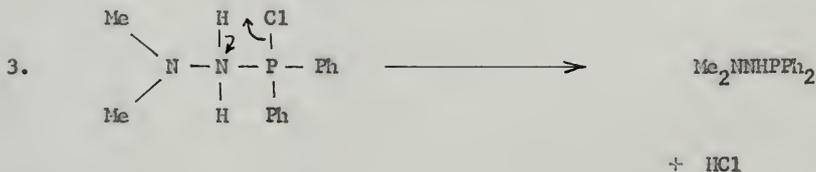
of the hydrazine on the phosphorus as an initial step which can occur in either of two ways.

Examples:

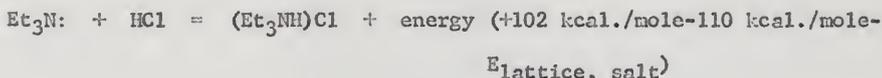


The energetics of this step would depend on the energy released by the formation of the P-N coordinate bond and the energy required to change the bond angles to that in the intermediate adduct. It is expected that this step would be reversible at low temperatures and that no further reaction would result from the adduct shown in equation 1.

The product from equation 2, however, could undergo intramolecular elimination of hydrogen chloride by a concerted electron transfer process as shown in equation 3:



The energetics of this step include breaking an N-H bond (+72 kcal./mole) and a P-Cl bond (+77 kcal./mole) and forming an H-Cl bond (-102 kcal./mole). This step is not favored by the thermodynamics of the process, but additional energy is released by the formation of salt produced when the evolved hydrogen chloride reacts with the free base provided for this purpose:



An alternate view, which is energetically identical, would involve the reaction of the labilized proton in the N-H bond of the adduct with the free base (+72 kcal./mole - 110 kcal./mole), followed by elimination of a chloride ion from the phosphorus intermediate (+77 kcal./mole) and subsequent salt formation ($-E_{\text{lattice, salt}}$).

The overall process, regardless of route, is described by the following thermodynamic equation:

$$\Delta E_{\text{reaction}} = (-E_{\text{adduct formation}}) + (+72 \text{ kcal.}) + (+77 \text{ kcal.}) + (-110 \text{ kcal.}) + (-E_{\text{lattice, salt}}) + (E_{\text{IP, EA}}).$$

$E_{\text{IP, EA}}$ includes the ionization potential and electron affinity corrections for the bond energies involved.

Inasmuch as the reaction is known to be spontaneous at room temperature, and since it is not thought that the adduct formation is of major importance energetically, the proton affinity for the amine and the lattice energy of the salt produced in the reaction make the largest contributions to the driving force of the reaction.

The fact that hydrazinolysis of a chlorophosphine oxide or sulfide is less vigorous than hydrazinolysis of a chlorophosphine may

be explained by considering 1) the availability of d-orbitals on the phosphorus (for adduct formation), 2) the size of the phosphorus atom and the space available for coordination of an attacking hydrazine molecule, and 3) the effect of an oxygen atom or sulfur atom as a substituent on the phosphorus atom.

The availability of d-orbitals on the phosphorus atom would be greater in phosphine sulfides than in phosphine oxides because of the higher electron density around the phosphorus atom in the oxides, which presumably results from the back-donation of electrons as described previously. Thus, the initial step in the mechanism, adduct formation, would be favored in phosphine sulfides over phosphine oxides on the basis of d-orbital availability.

The size of the phosphorus atom is sufficient to allow a coordination number of six in the hexafluorophosphate ion, PF_6^- , and five in the vapor phase form of phosphorus pentachloride and many organic derivatives which contain bulky groups. Thus, it is not expected that adduct formation of hydrazines with phosphines, phosphine oxides, or phosphine sulfides would be severely restricted by steric requirements. An order of reactivity, based on ease of access of a hydrazine molecule to the phosphorus atom, should be observed in which reactivity decreases in the series phosphines > phosphine oxides > phosphine sulfides.

High electron density is apparently the major effect favoring reactivity of chlorophosphorus compounds towards the solvolytic reaction. N.m.r. data indicate that the electron density about the phosphorus atom is greater in phosphine oxides than in phosphine

sulfides. Thus, by comparison with unoxidized phosphines, tetra-covalent chlorophosphorus compounds with oxygen as a substituent on the phosphorus atom should be deactivated towards hydrazinolysis less than would those with sulfur as a substituent.

In summarizing the various considerations affecting the hydrazinolysis reaction, it is suggested that d-orbital availability is not greatly affected by substituents on the phosphorus atom and that such orbitals are available whether or not the phosphorus is in the oxidized form, since the orbitals which participate in $d \pi - p \pi$ back-donation are not those which participate in adduct formation. Although steric considerations are in agreement with the observed reactivity, they are probably of minor importance. The major factor, high electron density about the phosphorus atom, is expected to labilize the chloride towards nucleophilic displacement or anionic elimination, which, in this particular system, appears to be an irreversible step.

Oxidation of hydrazinophosphines. Both phosphines and hydrazines are well-known for their reducing properties. Phosphines will, in general, react with oxygen to produce phosphine oxides, whereas hydrazines may be oxidized to a number of nitrogen-containing compounds, depending on the extent of oxidation and the system in which oxidation occurs. A great deal is yet to be learned concerning the direct oxidation of alkyl hydrazines.

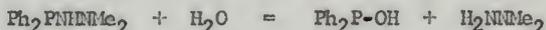
In the hydrazinophosphines it has been found that oxidation occurs preferentially on the phosphorus, and in this way some hydrazinophosphine oxides were prepared. Attack on the hydrazino-group also occurs, however, and in the case of 1-ethyl-2,2-dimethylhydrazinodiphenylphosphine complete decomposition was observed upon

prolonged exposure to dry, undiluted oxygen. Under milder oxidizing conditions it was found possible to prepare hydrazinophosphine sulfides by direct reaction of the hydrazinophosphine with elemental sulfur with undetectable effect on the hydrazino- group.

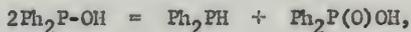
There is a basic difference in the mechanism of oxidation of phosphines and hydrazines: phosphorus may simply add an oxygen atom upon treatment with molecular oxygen; however, some N-N bonds are usually broken in the complex oxidation of hydrazines. The speed and simplicity of the phosphine oxidation is apparently the predominant reason for preferential reaction with oxygen and sulfur.

Hydrolysis of hydrazinophosphines. Hydrolysis of hydrazinophosphines occurs upon contact with moisture. It can be detected in samples by inspection of the infrared spectrum in the regions where the O-H and P=O absorption frequencies are found.

In the absence of oxygen, hydrolysis of 2,2-dimethylhydrazinodiphenylphosphine proceeds according to the equation below.



The diphenylphosphinous acid formed in this reaction undergoes a slow disproportionation as shown by the equation (73)

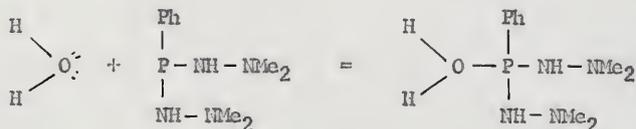


and it is for this reason that the hydrolysis can be detected by the presence of the intense P=O absorption frequency in the infrared.

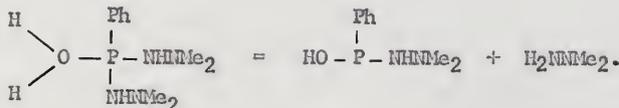
Atmospheric hydrolysis is accompanied by fast oxidation and the only observed product is diphenylphosphinic acid, $\text{Ph}_2\text{P(O)OH}$.

It was observed that bis(2,2-dimethylhydrazino)phenylphosphine is extremely susceptible to hydrolysis. The ease of hydrolysis is much greater than that observed for any monohydrazinophosphine. The effect is apparently due to the presence of two electronegative hydrazino- groups on the molecule.

The mechanism of hydrolysis follows the basic solvolytic process and presumably involves an initial attack of a water molecule on the phosphorus atom in the bis(hydrazino)phosphine as in the equation,



followed by the elimination of free 1,1-dimethylhydrazine as shown in the equation below:

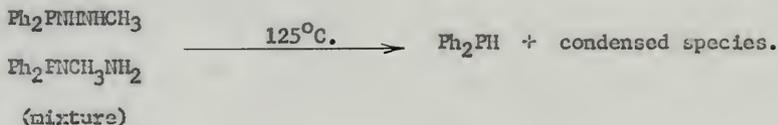


It is generally observed that as the number of electron-withdrawing groups on phosphorus is increased, the ease of solvolysis becomes greater; thus, it is not anomalous that bis(hydrazino)-phosphines, with two electronegative hydrazino-groups attached to the phosphorus atom should exhibit greater reactivity towards nucleophilic reagents than do monohydrazinophosphines.

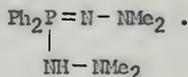
Hydrazinophosphine oxides and sulfides are, in general, more resistant towards hydrolysis than are the hydrazinophosphines. In

these instances, especially in the case of the oxides, the increased electron density about the phosphorus atom does not facilitate attack of nucleophilic reagents, such as water. The expected difference is noticed between $\text{Ph}_2\text{P}(\text{O})\text{NHNMe}_2$ and $\text{PhP}(\text{O})(\text{NHNMe}_2)_2$; the latter is less resistant towards hydrolysis.

Disproportionation of hydrazinophosphines. Inasmuch as diphenylphosphinous acid is known to disproportionate to diphenylphosphine and diphenylphosphinic acid (as described in the hydrolysis section), it might be anticipated that hydrazinophosphines would display similar behavior. Infrared and n.m.r. data have shown no evidence of disproportionation at room temperature, however, and only one hydrazinophosphine has shown such behavior at elevated temperatures:



In this reaction, the condensed species may be idealized as

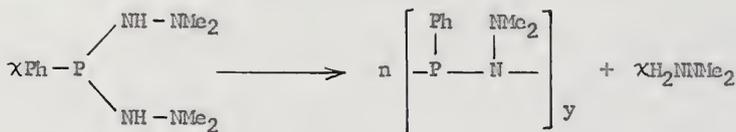


However, it was not possible to isolate this compound and it is probable that this species would undergo further condensation at the temperature required for the disproportionation.

Since it is the N-H bond which is broken when a hydrazine participates in hydrazinolysis, a hydrazinophosphine which contains

N-H bonds is subject to further reaction, with the N-H group acting as a nucleophilic reagent. It is observed that the reactivity of hydrazinophosphines increases with the number of N-H bonds in the molecule, thus while 2,2-dimethylhydrazinodiphenylphosphine ($\text{Ph}_2\text{PNHNMe}_2$) can be sublimed at 75°C . without serious loss by disproportionation, the methylhydrazinodiphenylphosphine mixture obtained by the reaction of methylhydrazine with chlorodiphenylphosphine is not separable by distillation because disproportionation occurs below the boiling point at 0.10 mm.

Condensation of hydrazinophosphines. Condensation of hydrazinophosphines by intermolecular elimination of hydrazines has been shown to occur at elevated temperatures. However, this behavior is much more evident in bis(hydrazino)phosphines than in the other hydrazinophosphines studied and occurs according to the following equation:



The evidence for other hydrazinophosphines undergoing a similar reaction is not conclusive enough to permit generalization at this point.

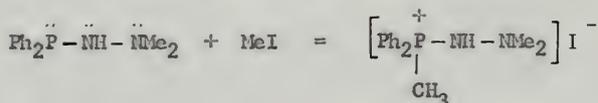
It is expected that condensation, rather than disproportionation, is the predominate high temperature reaction of most hydrazinophosphines. This effect should be most noticeable in those compounds in which the phosphorus atom possesses low electron density, which would facilitate nucleophilic attack of N-H groups

resulting in coupling and perhaps extensive polymerization of the hydrazinophosphines.

Alkylation of hydrazinophosphines. Alkylation of substituted hydrazinophosphines with methyl iodide has been shown to produce hydrazinophosphonium salts, rather than phosphinohydrazinium salts. The site of alkylation was determined by hydrolysis of the alkylation product to known phosphine oxide derivatives and the free hydrazine.

This result is particularly interesting in view of the fact that a study comparing the base strengths of phosphines and amines by titration with acids in non-interacting solvents indicates that, with respect to certain acids, amines are stronger bases than are similarly substituted phosphines (74). In addition, phenyl phosphines are among the least basic of the phosphines studied. The low basicity of phenyl phosphines is attributed to 1) steric effects and 2) pi-bond formation between the ring and the phosphorus atom.

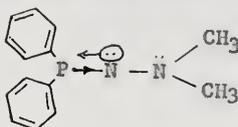
The alkylation of 2,2-dimethylhydrazinodiphenylphosphine with methyl iodide proceeds as given in the following equation:



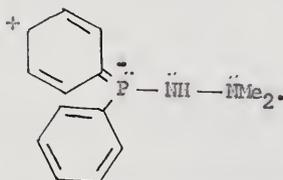
In 2,2-dimethylhydrazinodiphenylphosphine there are three possible sites capable of nucleophilic attack on methyl iodide by (presumably) the $\text{S}_{\text{N}}2$ mechanism. Although n.m.r. data which would indicate quantitatively the electron density about the phosphorus atom in 2,2-dimethylhydrazinodiphenylphosphine are not available,

it is thought that the electron density at the phosphorus atom in this molecule is greater than that in hydrazinophosphine oxides and sulfides.

Since alkylation occurs at the phosphorus atom, this is apparently the most electron-rich site in the molecule. The question arises regarding possible contributions of electron density from substituents on the phosphorus atom in hydrazinophosphines. The diphenylphosphino- group has been shown to be an electron-donating group towards the hydrazino- group in hydrazinophosphines. Thus, there is some polarization of the P-N bond in hydrazinophosphines, which may be compensated for by back-donation of electron density from the non-bonding electron pair on the nitrogen atom to the available d-orbitals on the phosphorus atom.



Further contribution to the electron density about the phosphorus atom may come from the phenyl rings which are in conjugation with each other and with the P-N bond:



Either or both of these contributions would allow the phosphorus atom to achieve the basicity necessary for successful attack on methyl

iodide. The nitrogen atoms in this molecule are apparently unable to increase their basicity by such means and must rely on the inductive effects of their substituents, which appears insufficient to permit alkylation in the presence of tricovalent phosphorus.

Alkylation was attempted with methyl iodide on several hydrazinophosphine oxides and sulfides, but no reaction was observed. The oxidized forms of hydrazinophosphines apparently do not possess the basicity at either of the nitrogen atoms necessary for nucleophilic attack on methyl iodide. This would serve to indicate that the diphenylphosphono- and diphenylphosphorothiono- groups are electron-withdrawing groups with respect to the hydrazino- groups, since alkyl hydrazines are quite easy to alkylate with methyl iodide.

No study was made of the effect of the solvent in these reactions and further work is indicated in this area.

Conclusion

The work reported here describes a series of new chemical species: substituted hydrazinophosphines, hydrazinophosphine oxides, hydrazinophosphine sulfides, and various derivatives of these compounds. These materials were characterized by elemental analysis, infrared spectral studies, nuclear magnetic resonance data, and observations of the reaction conditions and results.

Multiple substitution of diphenylphosphino-groups for protons on various hydrazines were carried out by the general hydrazinolysis reaction, thus synthesizing for the first time mono-, di-, and tri-phosphorus substituted hydrazines.

The reactions of the new compounds were studied, and special emphasis was placed on oxidation, hydrolysis, condensation, disproportionation, and alkylation of the new hydrazinophosphines.

Extensive data were collected which provide information concerning the electronic arrangements about the phosphorus atoms in these compounds, and general statements concerning the expected behavior of hydrazinophosphines can now be made. The diphenylphosphino group was found to act as an electron-donating group in hydrazinophosphines, whereas the diphenylphosphono- and diphenylphosphorothiono- groups are apparently electron-withdrawing in these compounds.

The hydrazinophosphines are more reactive towards nucleophilic reagents than are hydrazinophosphine sulfides and hydrazinophosphine oxides, which are less reactive in similarly substituted compounds. Thus, the hydrazinophosphine oxides are resistant to hydrolysis, condensation, and attack by electron-rich reagents, whereas more reactivity is to be expected for hydrazinophosphines and hydrazinophosphine sulfides.

The bis(hydrazino)phenylphosphines are found to be highly reactive, presumably as a result of the presence of the two electro-negative hydrazino- groups on the phosphorus atom. Consequently, these compounds are difficult to obtain in high purity and are extremely sensitive to atmospheric moisture and oxygen.

The results of this study have been correlated with current hypotheses concerning the relationships between molecular structure and chemical properties.

BIBLIOGRAPHY

1. Rochow, Hurd, and Lewis, The Chemistry of Organometallic Compounds, J. Wiley & Sons, Inc., New York (1957).
2. G. E. Coates, Organo-Metallic Compounds, J. Wiley & Sons, Inc., New York (1960).
3. H. Zeiss, Editor, Organometallic Chemistry (A. C. S. Monograph No. 147), Reinhold Publishing Co., New York (1960).
4. Advances in Chemistry Series, Metal-Organic Compounds, American Chemical Society, Washington, D. C. (1959).
5. D. R. Martin, Chem. Revs., 42, 581 (1948).
6. D. R. Martin, ibid., 34, 461 (1944).
7. H. S. Booth and D. R. Martin, Boron Trifluoride and Its Derivatives, J. Wiley & Sons, Inc., New York (1949).
8. N. N. Greenwood and R. L. Martin, Quart. Revs., 8, 1 (1954).
9. A. B. Burg, Record Chem. Prog. (Kresge-Hooker Sci. Library), 15, 159 (1954).
10. F. G. A. Stone, Quart. Revs., 9, 174 (1955).
11. M. F. Lappert, Chem. Revs., 56, 959 (1956).
12. F. G. A. Stone, ibid., 58, 161 (1958).
13. E. Krause and B. Went, Ber., 56, 466 (1923).
14. E. B. Baker and H. H. Sisler, J. Am. Chem. Soc., 75, 4828 (1953).
15. E. B. Baker and H. H. Sisler, ibid., 75, 5193 (1953).
16. N. Davidson and H. C. Brown, ibid., 64, 316 (1942).
17. A. W. Laubengayer, J. D. Smith, and G. G. Ehrlich, ibid., 83, 542 (1961).
18. G. Bahr, Fiat Review of German Science, 1939-1946, 24, Inorganic Chemistry, 155.

19. I. Zakharkin and L. A. Savina, Bull. Acad. Sci. U.S.S.R., 420 (March, 1957).
20. W. G. Paterson and M. Onyszchuk, Canad. J. Chem., 39, 2324 (1961).
21. N. R. Fetter and B. Bartocha, ibid., 39, 2001 (1961).
22. J. K. Ruff and M. F. Hawthorn, J. Am. Chem. Soc., 82, 2141 (1960).
23. E. Wiberg, H. Graf and R. Uson, Z. anorg. u. allgem. Chem., 272, 221 (1953).
24. E. Wibert and A. May, Z. Naturforsch. 10b, 234 (1955).
25. F. M. Peters and B. Bartocha, Chem. and Ind., 1272 (1961).
26. E. Krause and P. Dittman, Ber., 63, 2401 (1930).
27. G. Schomburg and E. G. Hoffman, Z. Elektrochem. Ber. Bunsenges Physik Chem., 61, 1110 (1957).
28. J. K. Ruff and M. F. Hawthorn, J. Am. Chem. Soc., 83, 535 (1961).
29. J. K. Ruff, ibid., 83, 2825 (1961).
30. A. W. Laubengayer, Inorganic Polymers (Special Publication No. 15), p. 78, The Chemical Society (London) (1961).
31. G. Schwarzenbach, Titrations with Complexones, Uetikon Chemical Co., Uetikon, Switzerland (1953).
32. G. M. Kosolapoff, Organophosphorus Compounds, J. Wiley & Sons, New York (1950).
33. J. R. Van Wazer, Phosphorus and Its Compounds, Vol. I, Interscience Publishers, Inc., New York (1958).
34. A. W. Frank, Chem. Revs., 61, 389 (1961).
35. E. G. Rochow, Editor, Inorganic Syntheses, Vol. VI, p. 108, McGraw-Hill Book Co., New York (1960).
36. A. B. Burg and P. J. Slota, J. Am. Chem. Soc., 80, 1107 (1958).
37. Fritz Ephraim and M. Sackheim, Ber., 44, 3416 (1911).
38. E. H. Blair and H. Tolkmith, J. Org. Chem., 25, 1620 (1960).
39. W. Autenrieth and W. Meyer, Ber., 58, 848 (1925).

40. A. Michaelis, Ann., 326, 129 (1903).
41. T. W. Mastin, G. R. Norman and E. A. Weilmuenster, J. Am. Chem. Soc., 67, 1662 (1945).
42. Shou Tung and Shyh-Tsong Chern, Hua Hsueh Hsueh Pao, 24, 30 (1958). (C. A. 52, 19903g; 53, 31131)
43. R. Klement and K. Knollmüller, Ber., 93, 834 (1960).
44. R. Klement and K. Knollmüller, Ber., 93, 1088 (1960).
45. A. G. Zenkevich, P. G. Zaks, Ya. A. Mandelbaum and N. N. Melnikov, J. Gen. Chem. U.S.S.R., 30, 2298 (1960) (Eng.).
46. Etcyl Blair, U. S. 2,855,423, Oct. 7, 1958.
47. Howard M. Titch, U. S. 2,759,961, Aug. 21, 1956.
48. A. Michaelis, Ann., 293, 193 (1896).
49. A. Michaelis, Ann., 293, 261 (1896).
50. W. C. Smith, R. Gher, Jr., and L. F. Audrieth, J. Org. Chem., 21, 113 (1956).
51. A. Michaelis, Ann., 294, 1 (1897).
52. W. Strecker and H. Heuser, Ber., 57, 1364 (1924).
53. W. Autenrieth and O. Hildebrand, Ber., 31, 1094 (1898).
54. Etcyl Blair, U. S. 2,885,424, Oct. 7, 1958.
55. A. W. Hofmann, Ann. Suppl., 1, 1 (1861).
56. W. C. Smith and L. F. Audrieth, J. Org. Chem., 22, 265 (1957).
57. R. J. Otto and L. F. Audrieth, J. Am. Chem. Soc., 80, 3575 (1958).
58. W. Couldridge, J. Chem. Soc., 53, 398 (1888).
59. H. H. Sisler, G. Omiotanski, and B. Rudner, Chem. Revs., 57, 1021 (1957).
60. Henery Tolkmith, U. S. 2,965,667, Dec. 20, 1960.
61. Class, et al., J. Am. Chem. Soc., 75, 2937 (1953).
62. Klages, Nober, et al., Ann., 547, 1 (1941).

63. R. H. Pierson, A. N. Fletcher and E. St. Clair Gantz, Anal. Chem., 28, 1213 (1956).
64. Backer, Rec. trav. chim., 31, 150 (1912).
65. Beacon Chemical Industries, Inc., 33 Richdale Avenue, Cambridge 40, Massachusetts.
66. D. D. Coffman and S. S. Marvel, J. Am. Chem. Soc., 51, 3496 (1929).
67. H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago and N. L. Smith, J. Am. Chem. Soc., 81, 2982 (1959).
68. K. A. Jensen, J. prakt. Chem., 148, 107 (1937).
69. T. N. Garbulis and D. H. Templeton, J. Am. Chem. Soc., 83, 995 (1961).
70. Heilbron, Dictionary of Organic Compounds, Vol. IV, p. 139, Oxford University Press, New York (1953).
71. L. J. Bellamy, The Infra-red Spectra of Complex Molecules, John Wiley & Sons, Inc., New York (1960).
72. R. A. McIvor and C. E. Hubley, Canad. J. Chem., 37, 869, (1959).
73. Victor Chemical Works (Chicago), Technical Bulletin: Diphenylphosphinous Chloride (1952).
74. W. A. Henderson, Jr., and C. A. Streuli, J. Am. Chem. Soc., 82, 5791 (1960).

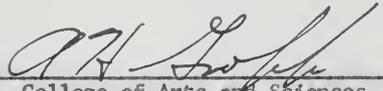
BIOGRAPHICAL SKETCH

Robert Peter Nielsen was born March 14, 1937, at New Brunswick, New Jersey. He received his elementary education in the public school system in Highland Park, New Jersey, and was graduated from Highland Park High School in 1954. In June, 1958, he received the degree of Bachelor of Science from Rutgers, The State University. In 1958, he enrolled in the Graduate School of the University of Florida. He worked as a graduate assistant in the Department of Chemistry until June, 1959, and as a teaching assistant until June, 1960. From June, 1960, until the present time he has pursued his work toward the degree Doctor of Philosophy as a research fellow under a grant from the Petroleum Research Fund administered by the American Chemical Society.

Robert Peter Nielsen is married to the former Linda Ray Galbraith. He is a member of the American Chemical Society, The Chemical Society (London), Phi Lambda Upsilon, and Sigma Xi.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

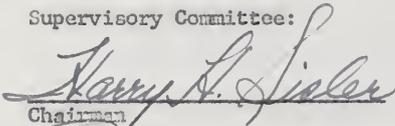
June 11, 1962



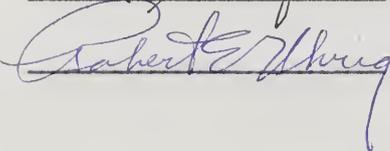
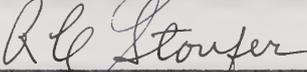
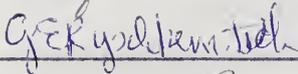
Dean, College of Arts and Sciences

Dean, Graduate School

Supervisory Committee:



Chairman



334091