69-7606

PASTERNACK, George, 1937-
ULTRAVIOLET ABSORPTION SPECTRA OF VINYLARSINES AND VINYLPHOSPHINES.

The City University of New York, Ph.D., 1969
Chemistry, organic

University Microfilms, Inc., Ann Arbor, Michigan

ULTRAVIOLET ABSORPTION SPECTRA
OF
VINYLARSINES AND VINYLPHOSPHINES

by

GEORGE PASTERNACK

A dissertation submitted to the
Graduate Faculty in Chemistry in partial
fulfillment of the requirements for the
degree of Doctor of Philosophy,
The City University of New York.

1968

This manuscript has been read and accepted for the University Committee in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

7/31/68
date

Michael A.
Chairman of Examining Committee

Aug. 31, 1968
date

Richard H. Wiley
Executive Officer

Michael A.

Saul

David E. Goldberg
Supervisory Committee

The City University of New York

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Professor Michael Wiener, who suggested the problem and gave his time willingly and enthusiastically during the entire course of this research. His advice and criticism were indeed invaluable.

Thanks are due also to Professor T. Haines for use of his gas chromatography apparatus, to Professor L. Schwartz, who kindly made available necessary laboratory apparatus, and to Professor N. McKelvie for his advice.

Finally, the author wishes to thank his sister, Sylvia, and his fiancee, Miriam, for their eagerness to type this manuscript.

TABLE OF CONTENTS

Page

ACKNOWLEDGEMENT ii

LIST OF TABLES v

LIST OF DIAGRAMS vii

LIST OF EXPERIMENTS viii

THE ULTRAVIOLET ABSORPTION SPECTRA OF PHOSPHORUS AND ARSENIC COMPOUNDS - HISTORICAL 1

INTRODUCTION 26

PART I.

RESULTS AND DISCUSSION 29

EXPERIMENTAL DISCUSSION 41

Preparation of Vinylarsines 41

Preparation of Vinylphosphines 45

Preparation of Vinylarsine and Vinylphosphine Oxides 49

PART II.

RESULTS AND DISCUSSION 71

EXPERIMENTAL DISCUSSION 74

Preparation of Trans-1,2-Vinylenebis(di-n-butylphosphine) 75

Preparation of Cis-1,2-Vinylenebis(di-n-butylphosphine) 76

Preparation of Tetraethylbiarsine 76

Preparation of Trans-1,2-Vinylenebis(di-n-butylphosphine) Monoxide 76

Preparation of Di-n-butylmethyl(trans-2-di-n-butylphosphinoxy)vinylphosphonium Iodide 78

Preparation of Trans-1,2-Vinylenebis(di-n-butylmethylphosphonium) Diiodide 78

Page

Preparation of Di-n-butylmethyl(trans-2-di-n-butylphosphinoxy)vinylphosphonium Bromide 78

Preparation of Trans-1,2-Vinylenebis(di-n-butylphosphine) Dioxide 78

Attempted Preparation of Di-n-butylmethyl(trans-β-di-n-butylphosphino)vinylphosphonium Bromide 81

APPENDIX 100

BIBLIOGRAPHY 101

AUTOBIOGRAPHICAL STATEMENT 106

LIST OF TABLES

Table	Title	Page
I	GAS PHASE VACUUM ULTRAVIOLET SPECTRA OF INORGANIC ARSINES AND PHOSPHINES	3
II	GAS PHASE ULTRAVIOLET SPECTRA OF PHOSPHINES	4
III	ULTRAVIOLET SPECTRA OF ACETYLENIC PHOSPHINES	5
IV and V	ULTRAVIOLET SPECTRA OF ARYL PHOSPHORUS AND ARSENIC COMPOUNDS	7
VI	ULTRAVIOLET ABSORPTION SPECTRA OF ORGANOPHOSPHINES	9
VII	ULTRAVIOLET ABSORPTION SPECTRA OF TOLYLPHOSPHINES	11
VIII	DIPOLE MOMENTS OF P-SUBSTITUTED ARYLPHOSPHINES	15
IX	INFRARED ARYL "C-C" BOND STRETCHING FREQUENCIES	15
X	ULTRAVIOLET ABSORPTION SPECTRA OF P-SUBSTITUTED PHOSPHINES	16
XI	ULTRAVIOLET SPECTRA OF SUBSTITUTED PHOSPHINES AND AMINES	19
XII	ULTRAVIOLET ABSORPTION SPECTRA OF ARYLARSINES	23
XIII	ULTRAVIOLET ABSORPTION SPECTRA OF ARYLPHOSPHINES	25
XIV	ULTRAVIOLET ABSORPTION SPECTRA OF VINYLARSINES	30
XV	ULTRAVIOLET ABSORPTION SPECTRA OF VINYLPHOSPHINES	31
XVI	VACUUM ULTRAVIOLET SPECTRA OF VINYL PHOSPHINES	35

Table	Title	Page
XVII	ULTRAVIOLET ABSORPTION SPECTRA OF VINYLBORANES	35
XVIII	ULTRAVIOLET ABSORPTION SPECTRA OF ORGANO SULFIDES	37
XIX	PREPARATION OF VINYLARSINES	44
XX	PREPARATION OF VINYLPHOSPHINES	48
XXI	ULTRAVIOLET ABSORPTION SPECTRA OF VINYLENE BIS(DI-N-BUTYLPHOSPHINES) AND RELATED COMPOUNDS	73

LIST OF DIAGRAMS

Figure	Description	Page
I	DIPOLE MEASUREMENT OF TRIARYLPHOSPHINES ...	10
II	IMPROVED METHOD FOR MEASURING DIPOLE MOMENTS OF TRIARYLPHOSPHINES	12
III	OVERLAP OF PHOSPHORUS d_{xz} ORBITAL WITH ETHYLENE π^* ORBITAL	39
IV	EXPECTED NMR SPECTRUM OF TRANS-1,2-VINYLENEBIS(DI-N-BUTYLPHOSPHINE) MONOXIDE .	79
V	EXPECTED NMR SPECTRUM OF TRANS-1,2-VINYLENEBIS(DI-N-BUTYLPHOSPHINE) DIOXIDE ..	80
VI	NONEQUIVALENCE OF HYDROGEN ATOMS IN CIS- AND TRANS-1,2-VINYLENEBIS(DI-N-BUTYLPHOSPHINE) DIOXIDE	81

LIST OF EXPERIMENTS

PART I

Page

EXPERIMENTAL

Purifications of Solvents 50

Preparation of Tri-n-butylvinyltin 50

Preparation of Phenyllithium 51

Preparation of Vinyllithium 51

Preparation of Vinylmagnesium Bromide 51

ARSENIC COMPOUNDS

Preparation of Arsenic Triodide 51

Preparation of Divinyliodoarsine 51

Preparation of Vinyldiiodoarsine 52

Preparation of Perfluoro-n-propyldivinylarsine 53

Preparation of Methyldivinylarsine 54

Preparation of Ethyldivinylarsine 54

Preparation of n-Butyldivinylarsine 55

Preparation of Dimethyliodoarsine 55

Preparation of Diethylbromoarsine 56

Preparation of n-Butylarsonic Acid 56

Preparation of n-Butyldibromoarsine 57

Preparation of Di-n-butylarsinic Acid 57

Preparation of Di-n-butylbromoarsine 58

Preparation of Dimethylvinylarsine 58

Preparation of Diethylvinylarsine 59

Preparation of Di-n-butylvinylarsine 59

Page

Preparation of Trivinylarsine 59

Preparation of Phenyldivinylarsine 60

PHOSPHORUS COMPOUNDS

Preparation of Thiophosphoryl Chloride 60

Preparation of Tetraethylbi(phosphine sulfide) 61

Preparation of Diethylthiophosphinyl Chloride 61

Preparation of Diethylchlorophosphine 62

Preparation of Ethyldichlorophosphine 62

Preparation of Di-n-butylcadmium 63

Preparation of n-Butyldichlorophosphine 63

Preparation of Di-n-butylchlorophosphine 63

Preparation of Ethyldivinylphosphine 64

Preparation of Diethylvinylphosphine 65

Preparation of n-Butyldivinylphosphine 65

Preparation of Di-n-butylvinylphosphine 65

Preparation of Trivinylphosphine 66

Preparation of Phenyldivinylphosphine 66

PREPARATION OF OXIDES

Preparation of Di-n-butylvinylphosphine Oxide 67

Preparation of Trivinylphosphine Oxide 67

Preparation of n-Butyldivinylarsine Oxide 68

Preparation of Diethylvinylarsine Oxide 69

PART II

EXPERIMENTAL

Page

Preparation of Tetra-n-butylbi(phosphine sulfide) .. 83

Preparation of Di-n-butylphosphine 83

Preparation of Lithium Di-n-butylphosphide 84

Preparation of Tetra-n-butylbiphosphine 84

Preparation of Trans-1,2-Vinylenebis(di-n-butylphosphine). Method A. Ether as Solvent 85

Preparation of Trans-1,2-Vinylenebis(di-n-butylphosphine). Method B. Tetrahydrofuran as Solvent 86

Preparation of Bis-1,2-Vinylenebis(di-n-butylphosphine). Method A. Ether as Solvent 88

Preparation of Cis-1,2-Vinylenebis(di-n-butylphosphine). Method B. Tetrahydrofuran as Solvent 89

Preparation of Mono-ethynylmagnesium Bromide 90

Preparation of Di-n-butylethynylphosphine 90

Preparation of Di-n-butylethynylphosphine Oxide 91

Preparation of Trans-1,2-Vinylenebis(di-n-butylphosphine) Monoxide. Method A. Via Reaction Between Di-n-butylethynylphosphine Oxide and Di-n-butylphosphine 91

Preparation of Di-n-butylphosphine Oxide 93

Preparation of Trans-1,2-Vinylenebis(di-n-butylphosphine) Monoxide. Method B. Via Reaction Between Di-n-butylethynylphosphine and Di-n-butylphosphine Oxide 93

Prepration of Trans-1,2-Vinylenebis(di-n-butylphosphine) Dioxide. Method A. Via Trans-1,2-Vinylenebis(di-n-butylphosphine) Monoxide and Hydrogen Peroxide 94

Preparation of Trans-1,2-Vinylenebis(di-n-butylphosphine) Dioxide. Method B. Via Trans-1,2-Vinylenebis(di-n-butylphosphine) and Hydrogen Peroxide 95

Page

Preparation of Trans-1,2-Vinylenebis(di-n-butylmethylphosphonium) Diiodide 96

Preparation of Di-n-butylmethyl(trans-β-di-n-butylphosphinoxy)vinylphosphonium Iodide 96

Preparation of Di-n-butylmethyl(trans-β-di-n-butylphosphinoxy)vinylphosphonium Bromide 97

Reaction of Di-n-butylmethyl(trans-β-di-n-butylphosphinoxy)vinylphosphonium Bromide with Trichlorosilane 97

Reaction of Di-n-butylmethyl(trans-β-di-n-butylphosphinoxy)vinylphosphonium Bromide with Phenylsilane . 98

Preparation of Diethylarsine 98

Preparation of Tetraethylbiarsine 98

THE ULTRAVIOLET ABSORPTION SPECTRA

OF

PHOSPHORUS AND ARSENIC COMPOUNDS

HISTORICAL

HISTORICAL

Although the literature contains a great deal of information on aliphatic and aromatic arsine and phosphine derivatives, until recently very little was known about the role of the lone pair of electrons and the d-orbitals on the central atom in chemical bonding. One method for obtaining such information is ultraviolet absorption spectroscopy. Most organic derivatives of tervalent arsenic and phosphorus absorb in the near ultraviolet, thus making this a very useful method.

Humphries[1] has studied some inorganic arsines and phosphines (see Table I). He found that in the vacuum ultraviolet region, all of the compounds exhibited a typical Rydberg type absorption pattern. Each gas phase spectrum consisted of a series of absorption peaks which converged to form a continuous band-pattern at higher energies. The longest single wavelength peak recorded varied from 1564 A (PF_3) to 1830 A (AsH_3). The other members of this series displayed their longest wavelength intermediate between the two values cited above.

Another investigator, Halman,[2] studied the gas-phase spectra of various phosphines in the region from 1850 A to 2500 A (see Table II). He suggested that the observed absorption was due to a transition of an electron on phosphorus to an antibonding molecular orbital (rather than to a phosphorus atomic orbital). This type of transition is analogous to those found in studies on compounds such as alkyl ethers and amines.[3]

A literature search failed to produce any reported study of trialkylarsine or trialkylphosphine spectra except for that of trimethylphosphine.[2]

Table I[1]

Gas Phase Vacuum Ultraviolet Spectra of Inorganic Arsines and Phosphines

Compound	λ_{max}[a] A
PF_3	1564
PCl_3	1750
PH_3	1800
PD_3	1800
AsH_3	1830
AsD_3	1830

---

a) Table lists the longest wavelength recorded for each compound in vacuum ultraviolet region.

Table II[2]

Gas Phase Ultraviolet Spectra of Phosphines

Compound	λ_{max}[a] A	ϵ
PH_3	1910	3,400
CH_3PH_2	2010; 1960; 1870	130; 1,500
$(CH_3)_2PH$	1890	6,300
$(CH_3)_3P$	2010	18,800
PCl_3	2170	3,500
$(C_2H_5)_2PCl$	2400; 1940	b

---

a) Region studied from 1850 A to 2500 A.

b) Not reported.

Charrier et al.[4] prepared some substituted ethynyl phosphines and recorded their ultraviolet spectra (see Table III). No conclusions based on their ultraviolet spectra were made on the reported compounds.

Table III[4,5]

Ultraviolet Spectra of Acetylenic Phosphines

Compound	λ_{max}^{a} mμ (ϵ x 10^{-3})				
$(C_2H_5)_2P-C\equiv C-C_6H_5$	220(12)	237(12)	237(13)	258(12)	282(7.5)
$(C_6H_5)_2P-C\equiv C-C_6H_5$	230(16)	246(16)	254(19)	265(19)	287(3.6)
$(C_6H_5)_2P(O)-C\equiv C-C_6H_5$	230(18)	244(18)	252(23)	264(19)	286(1.8)
$(C_6H_5)_2P(S)-C\equiv C-C_6H_5$	229(21)	254(21)	252(23)	264(18)	285(8)
$(C_2H_5)_2P-C\equiv C-$	219(12)	229(11)	240(10)	252(9)	
$(C_6H_5)_2P-C\equiv C-$		231(11)	253(9)	255(8)	
$(C_6H_5)_2P(O)-C\equiv C-$		229(16)	242(9)	252(9)	
$(C_6H_5)_2P(S)-C\equiv C-$		228(12)	241(10)	252(8)	

---

a) Spectra taken in ethanol.

The spectra of arylphosphines and arsines started to appear in the literature with the work of Bowden[6] and Jaffe[7] (see Tables IV and V). Both investigators reported that the tervalent derivatives had only one absorption peak in the region of 236-260 mμ ($\epsilon \leqslant 10^3$). However, when the lone pair of electrons was bonded, as in the corresponding oxides, onium halides or other related pentavalent compounds, the appearance of the spectra changed considerably. The spectra resembled that of benzene[*] or substituted benzenes in which the substituent(s) only slightly perturb the pi-electrons of the ring.

From the above data, Jaffe postulated that in the tervalent compounds the central atom was involved in the electronic transition. However, he did not have enough information to describe the actual mechanism of the transition. Increasing the number of phenyl substituents led to a shift toward longer wavelengths and increased intensity. This was attributed to conjugation of the phenyl groups attached to the central atom. Since the spectra of all the pentavalent compounds resembled that of benzene, Jaffe concluded that there was no conjugation in any of these compounds. He considered the ultraviolet spectra to be that of a slightly perturbed benzene system.

---

[*] Benzene has two regions of absorption in the near ultraviolet. a) 200 mμ ($\epsilon \sim 8000$); b) a series of weak bands centered at 260 mμ ($\epsilon \sim 200$). These two regions of absorption are commonly referred to as primary and secondary respectively.

Table IV[6]

Ultraviolet Spectra of Aryl Phosphorus and Arsenic Compounds

Compound	λ_{max} mμ	ε	Solvent
$C_6H_5P(CH_3)_2$	251	3600	Isooctane
$C_6H_5As(CH_3)_2$	239	6800	Isooctane
$C_6H_5As(CH_3)_2$	241	6800	Ethanol
$C_6H_5\overset{+}{P}(CH_3)_3\overset{-}{I}$	251, 260, 265, 272	450, 610, 920, 810	Ethanol
$C_6H_5\overset{+}{As}(CH_3)_3\overset{-}{I}$	250, 256, 262, 269	500, 600, 780, 670	Ethanol

Table V[7]

Ultraviolet Spectra of Aryl Phosphorus and Arsenic Compounds

Compound	λ_{max} mμ	ε (x 10^{-4})
$(C_6H_5)_3P$	261	1.10
$(C_6H_5)_3As$	268	1.23
$(C_6H_5)_3PO$	224.5, 260, 265.5, 272.5	2.14, 0.152, 0.196, 0.162
$(C_6H_5)_3AsO$	221, 258, 263, 270	2.16, 0.142, 0.172, 0.137
$C_6H_5AsO_3H_2$	214, 256.5, 262, 269	0.67, 0.0564, 0.0738, 0.0612
$C_6H_5PO_3H_2$		
$C_6H_5PO_2H_2$	216, 264	0.710 0.0616
$(C_6H_5)_2PO_2H$	224, 265	1.30 0.120
$(C_6H_5)_2PO^-$	222, 264	1.20 0.0882

In a subsequent study, Rao[8] correlated the spectra obtained by Jaffe with those of Bowden. He assigned the absorption band of the tertiary phosphines to an n-π^* transition. In this case the donor "n" electrons reside on the central atom and the π^* orbitals of benzene act as the acceptor orbital. Rao also postulated that the π^* orbitals of the phenyl groups were delocalized through conjugation. The increase in intensity and the lower transition energy of triphenylphosphine as compared to phenyldimethylphosphine (see Table IV) was attributed to the greater number of conjugated phenyl groups. He pointed out that triphenylphosphine has a lower transition energy than triphenylarsine due to the availability of 3d-orbitals on the phosphorus atom.[*]

Although Jaffe and Rao attempted to provide an explanation for the ultraviolet spectra, neither one clearly defined how these systems were conjugated nor did they distinguish conjugation in the ground state from conjugation in the excited state.

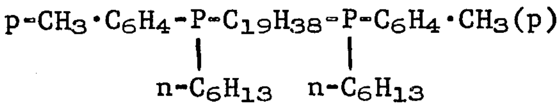
In 1962, Schindlbaur[9] extended the previously reported work to include a wide variety of alkylarylphosphines (see Table VI). He reaffirmed that the intensities of the peaks were dependent on the number of phenyl groups, and the wavelength of absorption varied with the nature of the alkyl substituents (as the electron donating power of the alkyl group increased, the transitional energy decreased). These results are in accord with the general interpretation of arylphosphine ultraviolet absorption spectra, proposed by Rao. He also recorded the ultraviolet spectra of phenylphosphine, p-ethylphenylphosphine and p-methylphenylphosphine

---

[*] It was presumed that the available 4d-orbitals or arsenic are too high in energy for this type of interaction.

Table VI[9]

Ultraviolet Absorption Spectra of Organophosphines

Compound	λ_{max} mμ	log ε
$(C_6H_5CH_2)_3P$	247	3.46
$C_6H_5P(CH_2CH_2CN)_2$	246	3.51
$(C_6H_5)_2PCH_2CH_2CN$	247	3.85
$(C_6H_5)_2PCH_2CH_2COOH$	248	3.79
$C_6H_5P(n\text{-}C_4H_9)_2$	251	3.44
$p\text{-}CH_3 \cdot C_6H_4P(i\text{-}C_4H_9)_2$	251	3.45
$C_6H_5P(i\text{-}C_4H_9)_2$	253	3.39
 $p\text{-}CH_3 \cdot C_6H_4\text{-}\underset{n\text{-}C_6H_{13}}{\underset{\vert}{P}}\text{-}C_{19}H_{38}\text{-}\underset{n\text{-}C_6H_{13}}{\underset{\vert}{P}}\text{-}C_6H_4 \cdot CH_3(p)$	256	3.73
$(C_6H_5)_3P$	262	4.02
$C_6H_5PCl_2$	264	3.23
$C_6H_5P(CH_3)_2$	266	3.35
$(C_6H_5)_2PC_6H_4P(C_6H_5)_2$	272	4.70
$C_6H_5PH_2$	234, 260, 265, 272	3.54, 2.8, 2.84, 2.72

and found that in all three cases the spectra consisted of an intense band at 220 mμ and a weaker band showing vibrational structure at 260-280 mμ. This retention of the benzene pattern is in sharp contrast to the effect of the amino group in aniline (strong peaks at 230 mμ and 290 mμ). Therefore, it appeared that in these compounds a π-π* transition (analogous to that found in benzene) was observed.

In a subsequent paper, Schindlbaur[10] observed a correspondence between the measured dipole moments and λ_{max} for a series of isomeric tritolylphosphines (see Table VII). It was concluded that these trends were a result of the changing of the C-P-C bond angle (ρ). The bond angles were presumed to increase from compound I and III due to repulsive interactions of the methyl substituents. As the molecule became more planar (θ → 90°), a decrease in the dipole moment would result (see Figure I). Flattening of the molecule would at the same time enhance the degree of π orbital overlap between the aryl substituents (via the phosphorus atom), thus lowering the excitation energy. Schindlbaur reasoned that these results were consistent with π-π* transition mechanism.

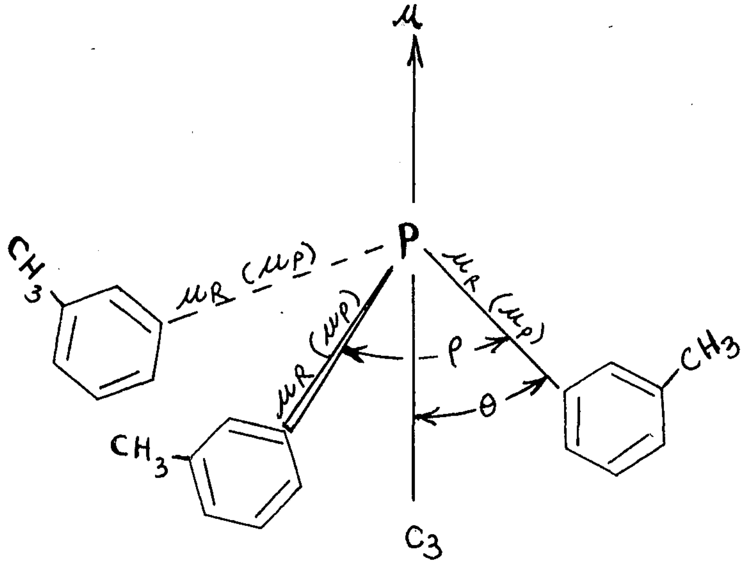


Figure I

Table VII[10]

Ultraviolet Absorption Spectra of Tolylphosphines

Compound	Dipole[a] moment μ (D)	Absorption Spectra[b] λ_{max}, mμ	log ε	Calculated C-P-C Bond Angle[c] Degrees
Tri(p-tolyl)phosphine (I)	2.14	262	4.06	100
Tri(m-tolyl)phosphine (II)	1.65	263	4.04	105
tri(o-tolyl)phosphine (III)	0.53	275	4.05	117

---

a) Taken in benzene at 20°.

b) Taken in 96% ethanol.

c) In calculating the C-P-C bond angles, Schindlbaur assumed that the molecule had C_{3v} symmetry and that μ_R (the group moment) was directed along the phosphorus-aryl bond moment (μp).

Mislow[11] has objected to Schindlbaur's treatment and has reinvestigated this work. Using a different model (see Figure II) Mislow rejected Schindlbaur's assumption of μ_R and μ_p being coincidental.

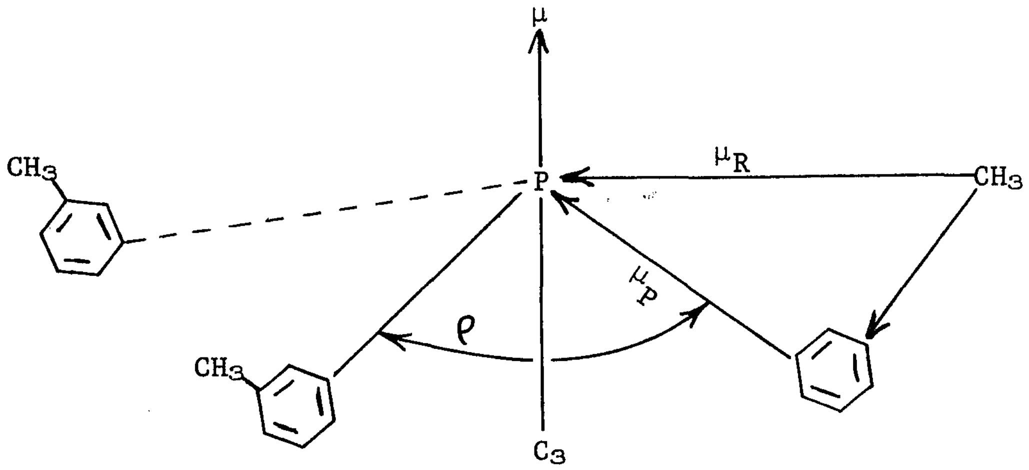


Figure II

Mislow assumed a constant bond angle (ρ = 102°) between the aryl groups. This assumption was based on the lack of significant variation of the X-P-X bond angles for a variety of tervalent phosphorus compounds.* He then proceeded to calculate the variation of the torsional angle around the phosphorus carbon bond with the change in dipole moment. Although Mislow did not investigate the nature of the electronic transition, he suggested that any overlap between the phosphorus atom and its aryl substituents was dependent on the torsional angle instead of the bond angle (ρ). Mislow also pointed out that the large difference of λ_{max} for the ortho substituted compound when compared to both the meta and para compounds, could be attributed to an inductive ortho effect. He prepared

---

*See article[11] for references therein.

tris(2,4,6-trimethylphenyl) phosphine and found that it absorbed at 312 mμ (log ε 4.20). This increased shifting toward the red was thought to be too large for simply a conjugative effect.

In a more extensive study, Goetz[12] attempted to elucidate the electronic distribution in both the ground and excited states of p-substituted arylphosphines:

$$(C_6H_5)_2PC_6H_4\text{-}Z(p)$$

where Z = H, Cl, Br, OCH_3, $N(CH_3)_2$.

The conclusions in this article were based on the information obtained from dipole moment measurements, infrared spectra and ultraviolet absorption spectra.

The trends observed in the dipole moment measurements led Goetz to suggest that in the ground state the electron density on the phosphorus atom was dependent on the electron donor ability of the p-substituents. As the substituent varies from chloro to amino (see Table VIII) charge is directed toward the phosphorus atom through the phenyl ring. This has the effect of increasing the charge density on both the phosphorus atom and the ring.

This shifting of electron density from the substituent toward the phenyl ring was confirmed by the infrared spectra of these compounds (see Table IX). The two aromatic infrared active bands at 1580 cm^{-1} and 1480 cm^{-1} have been assigned to vibrations of the phenyl ring.[13] The vibrational frequency of these bands is dependent on the "C-C" bond order of the ring. Therefore, a substituent which donates electrons into the ring would increase the bond order and thus raise the necessary vibrational energy.

The electronic distribution of the excited state was postulated from the ultraviolet absorption spectra. The region of absorption of the primary band in benzene did not show any trends within each series and so was not discussed. However, in the region of absorption of the secondary band of benzene a peak was observed whose position appeared to be substituent dependent (see Table X). The transition energy increased when the p-substituent varied in the order Cl < Br < OCH_3. Due to their low oscillator strength, these bands were assigned to an n-π* transition.

Ground State Excited State

With this assignment, Goetz reasoned that if the principal effect of the p-substituent was to shift electronic charge toward the phosphorus atom in the ground state (as shown by dipole measurements), then the frequency of maximum absorption should be in the opposite order to the one observed. The spectral trend was explained by considering that the effect of the substituent on the excited state must be more important than its effect on the ground state. Increasing the electron density on the ring in the excited state would destabilize the excited state of an n-π* transition. Goetz therefore concluded that the excited state must be destabilized by the substituents in the order CH_3O > Br > Cl.

Goetz also discussed the possibility of another n-π* transition where the para-substituent is the donor. This possibility was dismissed

Table VIII[12]

Dipole Moments of p-Substituted Arylphosphines

Compound	Dipole Moment Debyes[a]
$(C_6H_5)_3P$	1.42
$p\text{-}Cl\cdot C_6H_4\cdot P(C_6H_5)_2$	2.08
$p\text{-}Br\cdot C_6H_4\cdot P(C_6H_5)_2$	2.05
$p\text{-}CH_3O\cdot C_6H_4\cdot P(C_6H_5)_2$	2.55
$p\text{-}(CH_3)_2N\cdot C_6H_4\cdot P(C_6H_5)_2$	3.35

---

a) Taken in benzene at 20°.

Table IX[12]

Infrared Aryl "C-C" Bond Stretching Frequencies

Para-Substituent	Frequency cm^{-1}	
Br	a	a
Cl	1489	1481
H	1588	1478
CH_3	1599	1490
OCH_3	1599	1496
$N(CH_3)_2$	1604	1512

---

a) Not reported.

Table X[12]

Ultraviolet Absorption Spectra of p-Substituted Phosphines[a]

Para-Substituent	Frequency cm^{-1}	Oscillator Strength
H	37,900	0.28
Cl	37,700	0.35
Br	38,000	0.38
OCH_3	38,300	0.37

---

a) Taken in dioxane.

for the following two reasons: a) as the electron donor ability of Z increases the transition frequency should decrease which is opposite to the effect found. b) this type of transition would lead to a greater change in the dipole moment and so one would expect larger values for the oscillator strengths (f).

The p-dimethylaminophenyldiphenylphosphine exhibited only one peak, at 35,300 cm^{-1} (f = 0.54). This was ascribed to an overlapping of the phosphorus n → π* transition with an n → π* transition involving the lone pair of electrons on nitrogen. It was suggested that in this case the phosphorus n → π* transition was submerged under the nitrogen n → π* transition.

In this work, Goetz has attempted to distinguish between the ground state and the excited state of arylphosphines in terms of contributing resonance structures. Although he assigns the excitation to an n-π* transition, he does not propose an excited state in which there is any conjugation between phenyl groups. This latter point is in contrast to Rao's interpretation of the spectra of arylphosphines.

Another investigator, Schiemenz,[14] used the p-dimethylaminophenyl group as a probe to detect any conjugation between phosphorus and its aryl substituents.

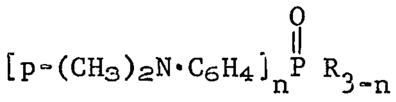
The following four groups of compounds were studied:

$[p\text{-}(CH_3)_2N\cdot C_6H_4]_n\overset{+}{P}\ R_{3-n}R\ X^-$

I

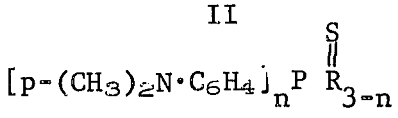
$[p\text{-}(CH_3)_2N\cdot C_6H_4]_n P\ R_{3-n}$

II



$[p\text{-}(CH_3)_2N\cdot C_6H_4]_n\overset{O}{\overset{\|}{P}}\ R_{3-n}$

III



$[p\text{-}(CH_3)_2N\cdot C_6H_4]_n\overset{S}{\overset{\|}{P}}\ R_{3-n}$

IV

The one peak observed for the compounds in group I had an extinction coefficient greater than 1 x 10^4. The extinction coefficient was proportional to the number of p-dimethylaminophenyl groups present, and in the case of the aryl derivatives, the absorption frequency was independent of the number of p-dimethylaminophenyl groups. From the above data, Schiemenz assigned the absorption peak to that of a p-substituted dimethylaminophenyl group.* The p-phosphonium substituent appears to bathochromically shift the more intense peak of N,N-dimethylaniline to almost the same extent as a carbomethoxy group (see Table XI).

This shift cannot be explained by an inductive effect of the positively charged phosphorus atom, for the spectrum of p-N,N-dimethylaminophenyltrimethylammonium iodide ($[p\text{-}(CH_3)_2N \cdot C_6H_4\overset{+}{N}(CH_3)_3]I^-$) does not show such a shift (see Table XI). Nor can the observed shift be attributed to conjugation of aryl groups on phosphorus. The independence of the wavelength of absorption with respect to the number of aryl groups precludes the possibility of conjugation.

The bathochromic shift of the organic chromophore was attributed to the available empty 3d-orbitals on phosphorus. Schiemenz proposed the formation of $d_\pi\text{-}p_\pi$ bonds between phosphorus and the organic substituent, leading to the lowering in energy of the aryl π-π^* transition. The spectra of the compounds in groups II, III and IV showed an intense peak in the same region of absorption as p-cyano-N,N-dimethylaniline with practically

---

*N,N-dimethylaniline exhibits two π-π^* transitions[9]. a) 38,500 cm^{-1} (log ϵ = 4.1; b) 22,360 cm^{-1} (log ϵ = 3.2). However, when substituted in the para position by an electron withdrawing group (e.g. CN, CO_2CH_3, CHO) only one peak is observed (see Table XI) with log $\epsilon > 4$. It appears that the bathochromically shifted intense peak now blots out the smaller, higher wavelength peak.

Table XI[14]

Ultraviolet Spectra of Substituted Phosphines and Amines

Compound	λ_{max}^{a} cm^{-1}	ϵ	ϵ/n^{b}
p-$(CH_3)_2NC_6H_4COOCH_3$	32400	27500	27500
p-$(CH_3)_2NC_6H_4\overset{+}{P}(C_6H_5)_2(CH_3)\ \ I^-$	33400	26300	26300
$[$p-$(CH_3)_2NC_6H_4]_2\overset{+}{P}(C_6H_5)(CH_3)\ \ I^-$	32900	45000	22500
$[$p-$(CH_3)_2NC_6H_4]_3\overset{+}{P}C_2H_5\ \ I^-$	33200	80800	26930
p-$(CH_3)_2NC_6H_4\overset{+}{N}(CH_3)_3\ \ I^-$	38000	22200	22200
p-$(CH_3)_2NC_6H_4\overset{+}{P}(CH_3)_3\ \ I^-$	35400	28400	28400
p-$(CH_3)_2NC_6H_4CN$	34400	26500	26500
p-$(CH_3)_2NC_6H_4P(C_6H_5)_2$	35400	27800	27800
p-$(CH_3)_2NC_6H_4P(O)(C_6H_5)_2$	35200	27300	27300
p-$(CH_3)_2NC_6H_4P(S)(C_6H_5)_2$	35000	21900	21900
$[$p-$(CH_3)_2NC_6H_4]_3P$	35100	70500	23500
$[$p-$(CH_3)_2NC_6H_4]_3P(O)$	35200	75000	25000
$[$p-$(CH_3)_2NC_6H_4]_3P(S)$	35000	21900	21900

---

a) Solvent used: Methanol.

b) n is the number of p-dimethylaminophenyl groups present.

the same extinction coefficient, indicating that the -M effect of phosphorus in these compounds was less than in the phosphonium compounds (see Table XI).

An attempt has been made to limit this discussion to tervalent compounds. However, for most papers cited it was necessary to discuss and compare the tervalent with the pentavalent compounds. There are many more reports in the literature that deal exclusively with the pentavalent compounds (oxides and onium salts).[15,16,17] Since these compounds are not necessarily relevant to the present study it should suffice to simply state the results and general conclusions reported.

In the compounds studied, the pentavalent phosphorus atom was bonded to either an aryl group which had powerful electron donor substituents or to a heteroaryl group (e.g. tri-2-pyrrylphosphine oxide) known to act as a powerful electron donor.

In all cases (oxides and onium salts) the presence of the pentavalent phosphorus atom shifted the absorption of the unsubstituted organic group to higher wavelengths. This bathochromic shift cannot be explained solely on the basis of an inductive effect by the phosphorus atom. In fact, it is generally agreed that the available empty d-orbirals on phosphorus are responsible for this effect.

The results of the papers cited may be summarized as follows.

1) When the phosphorus atom is substituted with a phenyl group containing a strong electron-donating substituent (e.g. NR_2) or when the phosphorus atom is substituted with an organic moiety which acts as a powerful electron donor, there results an interaction between the phosphorus atom and the organic group. This interaction is believed to be due to d_π-p_π bonding. The positively charged phosphorus atom in pentavalent compounds

enhances this type of interaction and therefore d_π-p_π bonding is more significant in pentavalent phosphorus compounds than in tervalent compounds.

2) When the phosphorus atom is bonded to a phenyl group which is either unsubstituted or substituted with groups not strongly electron donating (e.g. CH_3), there is very little d_π-p_π interaction between the phosphorus atom and its substituents. This lack of interaction appears to be independent of the oxidation state of the phosphorus atom.

3) When there is significant d_π-p_π interaction it manifests itself by shifting the ultraviolet absorption of the unsubstituted organic group to higher wavelengths.

4) The type of transition in the aryl tervalent phosphorus compounds seems to depend on the electron donor ability of the phenyl substituents. When the aryl group is substituted with strong electron donor substituents (e.g. NR_2), the observed transition is simply the π-π^* transition of the aryl group. If there is a transition occurring which involves the phosphorus lone pair of electrons, it is swamped out by the π-π^* transition. However, when the aryl group is unsubstituted or substituted with weak electron donors (e.g. CH_3), the transition has not been clearly defined. Rao and Goetz have suggested that these type of compounds undergo an n-π^* type of transition in which the lone pair of electrons on the phosphorus atom is the donor. Schindlbaur, on the other hand, suggests in his tolyl series that the compounds are undergoing a π-π^* transition.

From the above statements two things appear quite clear:

1) More information is needed before these transitions are well defined.

2) One cannot elucidate the transition mechanism for one class of phosphorus compounds and expect it to be applicable to all others. The type of substituents evidently play a major role in these transitions.

Up until the present study there were only two reports in the literature dealing with the ultraviolet spectra of tervalent arsines. Cullen and Hochstrasser[18] examined the ultraviolet spectra of several arylarsines (see Table XII). They observed two regions of absorption, one at 2700 A and the other at 2200-2500 A. The 2700 A absorption appeared as a series of sharp but weak bands. These bands barely appeared as shoulders on the main peak of triphenylarsine (2480 A), but when the more electronegative trifluoromethyl group(s) was substituted for phenyl group(s), the main band was shifted toward the blue enough to clearly separate both regions of absorption. The intensity and position of the 2700 A peaks closely resembled those of monosubstituted benzenes. In addition, the authors also demonstrated that these peaks exhibited small red shifts in polar solvents and that the extinction coefficients were approximately proportional to the number of phenyl groups. From the above data,the authors conluded that the absorption was due to a π-π^* transition analogous to that found in monosubstituted benzenes. From this spectral assignment,the existence of appreciable amounts of conjugation between the phenyl groups was ruled out.

The high energy absorption band was believed to be too intense to be a typical n-π^* transition.* It was pointed out that the overlap between the n and the π (2p) orbitals would be quite small and this would

---

*This is in contrast to the assumption made by Goetz.[12]

Table XII[18]

Ultraviolet Absorption Spectra of Arylarsines

Compound	λ_{max} A $(\epsilon \times 10^{-2})^{a}$	
$(C_6H_5)_3As$	2480(131)	2610, 2670, 2730(2.0)
$(C_6H_5)_2AsCF_3$	2240(9.0)2368(63)	2575, 2690, 2720(0.90)
$C_6H_5As(CF_3)_2$	2238(60)	2530, 2587, 2650, 2718(0.65)
$C_6H_5As(CH_3)CF_3)$	2210(50)	2500, 2565, 2630, 2700(0.50)
$(C_6H_5)_2AsCH_3$	2405(146)	2640(1.7) 2715(1.8)
$C_6H_5As(CH_3)_2$	2390(68)	

---

a) Taken in isooctane.

have led to a low extinction coefficient. Cullen and Hochstrasser therefore tentatively proposed a transition which they labelled an intramolecular charge-transfer excitation. This involves the transfer of one of the lone-pair of electrons on arsenic to a π^* orbital on a phenyl group, resulting in a charge-separated excited state. The electron is transferred through space and therefore is not overlap dependent as in an n-π^* transition.[*]

Recently Shaw[20] et al. have studied the ultraviolet absorption spectra of some arylphosphines (see Table XIII). They reported observing some weak bands appearing as shoulders on the main band. They attributed these weak bands to be due to the same benzene-like π-π^* transitions observed for arylarsines by Cullen and Hochstrasser.

---

[*] In pyridine, if the "n" electrons on nitrogen were in a pure p-orbital, then the transition moment integral "$\int \psi e M_{(x,y,z)} \psi g d\tau$" would be zero. However, if the "n" electrons have some "s" character then the integral is no longer equal to zero, and the n-π^* transition is observed. The extinction coefficient for this transition is approximately ($\epsilon = 10^2$).[19]

Table XIII[20]

Ultraviolet Absorption Spectra of Arylphosphines

Compound	λ_{max} mμ	ε	λ_{max} mμ	ε
$C_6H_5P(C_2H_5)_2$	252.8	3,300	273.2	140
$(C_6H_5)_2PC_2H_5$	251.3	8,090	277.8	950
$(C_6H_5)_3P$	261.4	11,000	281.7	1,250
$(C_6H_5)_2P(O)C_2H_5$			265.0	1,370

---

a) Spectra taken in ethanol.

INTRODUCTION

A significant difference exists between the various reported interpretations of arylarsine and arylphosphine spectra.[1-20] This lack of uniformity may be inherent in the type of systems chosen for study. Benzene and substituted benzenes have absorption bands in the investigated region (ca. 210-260 mμ). Therefore, one must be able to distinguish between a perturbed benzene band and one due to a totally new chromophoric species. It would be much more advantageous to discuss the origin of a peak in a region where the separate chromophores do not absorb at all.

In the present study, the ultraviolet absorption spectra of vinylarsines and vinylphosphines have been recorded and have been shown to exhibit a λ_{max} in the region 225-240 mμ. This is in contrast to the separate chromophores; the solution spectrum of ethylene has no peak above 180 mμ,[21] and the spectra of trialkylarsines and phosphines have no maximum above 210 mμ.[*] Therefore, a study of the spectra of the vinyl derivatives of arsenic and phosphorus should be useful in distinguishing among the different spectral interpretations of the aryl derivatives.

Evidence has been obtained in the first part of this study to show the absence of significant perturbative effects between the vinyl group and the arsenic or phosphorus atom. Moreover, on the basis of various spectral trends in the compounds studied, the observed transition has been assigned to a charge transfer mechanism. In this transition, one of the lone pair of electrons on the central atom is optically excited into the π* orbital of the vinyl group. Therefore, the observed transition effectively involves a new chromophoric species.

---

[*] See Tables II, XIV and XV.

Recently, chemical evidence has appeared in the literature[66-68] which suggests that a tervalent phosphorus atom is capable of stabilizing an alpha carbanion by electron withdrawal into its empty d-orbitals. In the second part of this study, spectroscopic evidence has been obtained to demonstrate the effectiveness of a tervalent (as well as a pentavalent) phosphorus atom in delocalizing an excess of charge. This investigation was suggested by the assignment made on the spectra of vinylphosphines. The excited state of these compounds is charge-separated, with the vinyl group becoming negatively charged. It appears from this study that substitution of a second phosphorus atom vicinal to the first provides additional stabilization of the excited state via an electron withdrawal mechanism.

Part I

RESULTS AND DISCUSSION

This is the first reported ultraviolet absorption spectral study on a series of air sensitive aliphatic phosphines and arsines in solution (Tables XIV and XV). Due to the extreme sensitivity of compounds of this nature, absorption spectra have in the past been taken in the gas phase. To insure the reliability of the spectral data, the more volatile compounds were measured in the gas phase (see Tables XIV and XV) and compared with their respective solution spectra. The spectra obtained on samples in the gas phase followed the same trends as the spectra obtained on the solutions. Therefore, the conclusions made in the following discussion, based upon the observed spectral trends, appear equally valid in solution and gas phases. However, λ_{max} for the gas phase spectra were generally lowered by *ca.* 5 mμ from the corresponding solution spectra. This hypsochromic shift from solution to gas phase spectra for n-π* type transitions has been discussed by Bayliss.[22]

Another indication of the reliability of the reported results concerns the precision with which the absorption intensities were obtained. The maximum deviation of any value of ϵ_{max} from the average of three determinations (obtained from three different solutions of the same compound) was ± 3%. In almost all cases, the deviation was less. The chief concern in taking solution spectra was the possible oxidation of the trivalent compounds. If oxidation was occurring, it would have undoubtably led to a series of inconsistent data. The similar trends exhibited by the solution and gas phase spectra, combined with the good precision in measured absorption intensities, seem to rule out any significant contamination of the sample.

Table XIV

Ultraviolet Absorption Spectra of Vinylarsines

Compound	Solvent[a]	λ_{max} mμ[b]	$(\epsilon_{max} \times 10^{-3})$[c]
$(CH_3)_2AsC_2H_3$	I	231	(3.07)
"	M	230	(3.03)
"	G	225	
$(C_2H_5)_2AsC_2H_3$	I	235	(2.81)
"	M	234	(2.83)
"	G	230	
$\underline{n}$-$(C_4H_9)_2AsC_2H_3$	I	236	(2.45)
$CH_3As(C_2H_3)_2$	I	228	(4.50)
"	M	227	(4.45)
"	G	223	
$C_2H_5As(C_2H_3)_2$	I	230	(4.27)
"	M	229	(4.02)
"	G	225	
$\underline{n}$-$C_4H_9As(C_2H_3)_2$	I	231	(3.99)
"	M	230	(4.04)
$\underline{n}$-$C_3F_7As(C_2H_3)_2$	I	ca. 215-220[d]	
"	G	ca. 215-220[d]	
$(C_2H_3)_3As$	I	227	(4.98)
"	M	227	(4.65)
"	G	222	
$(C_2H_5)_3As$	I	208	(11.7)
"	M	207	(10.4)
"	G	206	
$C_6H_5As(C_2H_3)_2$	I	232	(7.59)
$(C_2H_5)_2As(O)C_2H_3$	M[e]	---	
$\underline{n}$-$C_4H_9As(O)(C_2H_3)_2$	M[e]	---	

---

a) Isooctane (I), methanol (M), gas (G). b) Due to the broadness of the peak near the maximum, λ_{max} is reported only to the nearest mμ. c) Intensity data for the gas phase spectra were not obtained because of the lack of a suitable pressure-measuring device. d) Region of inflection. e) Most of the oxides obtained were insoluble in isooctane.

Table XV

Ultraviolet Absorption Spectra of Vinylphosphines

Compound	Solvent[a]	λ_{max} mμ[b]	(ϵ_{max} x 10^{-3})[c]
$(C_2H_5)_2PC_2H_3$	I	244	(2.71)
"	M	242	(2.76)
"	G	239	
n-$(C_4H_9)_2PC_2H_3$	I	246	(2.60)
"	M	245	(2.63)
$C_2H_5P(C_2H_3)_2$	I	237	(5.20)
"	M	236	(5.23)
"	G	231	
n-$C_4H_9P(C_2H_3)_2$	I	238	(5.13)
"	M	237	(5.25)
$(C_2H_3)_3P$	I	235	(6.41)
"	M	234	'6.48)
"	G	229	
n-$(C_4H_9)_3P$	I	204	(11.2)
"	M	203	(11.4)
$C_6H_5P(C_2H_3)_2$	I	242	(7.30)
n-$(C_4H_9)_2P(O)C_2H_3$	I	*ca.* 200[d]	
$(C_2H_3)_3PO$	M[e]	---	

---

a) Isooctane (I), methanol (M), gas (G). b) Due to the broadness of the peak near the maximum, λ_{max} is reported only to the nearest mμ. c) Intensity data for the gas phase spectra were not obtained because of the lack of a suitable pressure-measuring device. d) Region of inflection. e) Most of the oxides obtained were insoluble in isooctane.

Each of the trivalent vinyl derivatives exhibits a single peak in the ultraviolet region above 220 mμ, together with a second, intense absorption at shorter wavelengths which shows no maximum above 200 mμ. The longer-wavelength absorption peak disappears upon oxidation of the trivalent derivatives.* The absorption maxima for these longer wavelength bands are listed in Tables XIV and XV.

The data demonstrate rather clearly the dependence of λ_{max} on the electron-donating ability (inductive effect) of the groups attached to the central atom. For each series of compounds, $R_nM(C_2H_3)_{3-n}$, the wavelength of maximum absorption increases with R in the order $CH_3 < C_2H_5 < C_4H_9$. Moreover, successive replacement of alkyl groups by vinyl groups results in a decrease of λ_{max} in every case. In the spectrum of the one perfluoralkyl compound investigated, the absorption maximum was lowered so much by the electron withdrawing group that it appears only as a region of inflection on the intense, short-wavelength peak.

The sensitivity of the observed transition energy to the electron density on the central atom, and the disappearance of the observed band upon coordination of the lone pair of electrons (via oxidation) strongly suggest that the transition responsible for the longer-wavelength band involves an electron from the nonbonded orbital on the central atom. The relative transition energies are then influenced most importantly by the effect of the attached groups on the ionization energy of the lone pair of electrons. However, these transitions do not appear to be either a

---

*Popov[23] has recorded the vacuum ultraviolet spectra of di-n-butylphosphine and its oxide. The absorption maxima reported at 182 mμ (ϵ = 17,000) and 179 mμ (ϵ = 14,600) for the two compounds respectively.

Rydberg or n → σ* transition of the type postulated for $M(R)_3$ [M = As,P; R = H, alkyl].[1,2,24] Although only a few alkylphosphine or alkylarsine spectra have been recorded (see Tables II, XIV and XV), there is no evidence of any maximum above 210 mμ in the spectrum of any saturated derivative. In addition, the measured intensities for the saturated compounds are consistently higher than those measured for any vinyl derivative. Thus it appears likely that the π orbitals on the vinyl groups also play a role in this transition.

The solution ultraviolet absorption spectra of monosubstituted olefins exhibit a λ_{max} in the region between 180-190 mμ.[21] This has been assigned to a π-π* transition and it is readily recognized by its large extinction coefficient ($10^5 > \epsilon > 10^4$).

Matsen[25] has discussed the bathochromic effect of a substituent bearing a lone-pair of electrons on the π-π* transition of ethylene. This effect is due primarily to a conjugative interaction between the nonbonded orbital of the substituent (containing the lone-pair) and the π orbital of the vinyl group. It is highly unlikely that the absorption maximum observed in this study is an ethylenic π-π* transition shifted to longer wavelengths by this type of interaction. A bathochromic shift of at least 20-40 mμ would have to be postulated in this case, and this would seem to be unusually large. By way of comparison the ultraviolet spectra of simple enamines show no absorption maxima higher than 225-235 mμ,[26] in spite of the generally recognized importance of 2p - 2p π overlap between nitrogen and the attached unsaturated group.

The effective disappearance of the longer-wavelength absorption maximum upon oxidation of the tervalent compounds, would appear to eliminate the possibility that the band is actually an ethylenic π-π* transition sufficiently shifted by an inductive effect or some interaction involving the d-orbitals of the central atom. If anything, oxidation would enhance either of the two mentioned possible effects by increasing the electronegativity of the central atom.

Popov[23] has compared the vacuum ultraviolet spectra of vinylphosphines and their oxides with that of 1-hexene. In all cases an intense peak was observed around 180 mμ ($10^5 > \epsilon > 10^4$). The position of the observed band appeared to be independent of the nature of the substituents on the phosphorus atom (see Table XVI). The apparent lack of any effect due to the phosphorus atom led Popov to conclude that the observed band was the ethylene π-π^* transition.

Conjugation between the vinyl groups could account for a shift in the π-π^* band of ethylene. However, as the number of vinyl groups increase, the transition energy also increases (see Tables XIV and XV). This is contrary to the spectral trends expected for conjugated systems.

Ritter[27] has studied compounds of the general formula $(CH_3)_nB(C_2H_3)_{3-n}$. He found that as vinyl groups are substituted for methyl groups, the absorption energy decreases (see Table XVII). This is in agreement with a conjugated system of double bonds. By means of a Hückel molecular orbital calculation, Ritter showed that the energy difference between the highest filled and the lowest unfilled molecular orbitals decreased by increasing the number of vinyl groups. These calculations were based on the assumption that boron and the adjacent carbon atoms of the vinyl group(s) had an overlap integral comparable with β_{c-c}. This assumption appears reasonable on account of the planarity of simple tervalent boron compounds.

Table XVI[23]

Vacuum Ultraviolet Spectra of Vinyl Phosphines

Compound	λ_{max}[a] A	ϵ
$CH_2=CH-C_4H_9-n$	1800	11,000
$CH_2=CH-CH_2-(O)P(OC_4H_9)_2$	1820	11,000
$CH_2=CH-(O)PCl_2$	1780	11,700
$CH_2=CH-(O)P[N(CH_3)_2]_2$	1740	16,400
$CH_2=CH-(O)P(OC_4H_9)_2$	1770	13,400
$CH_2=CH-(O)P(C_4H_9)_2$	1790	14,600
$CH_2=CH-(O)PCH_3(OC_4H_9)$	1760	12,700
$CH_2=CH-P(OC_4H_9)_2$	1760	12,000
$CH_2=CH-P(C_4H_9)_2$	1820	17,000

---

a) Solvent used was heptane.

Table XVII[27]

Ultraviolet Absorption Spectra of Vinylboranes[a]

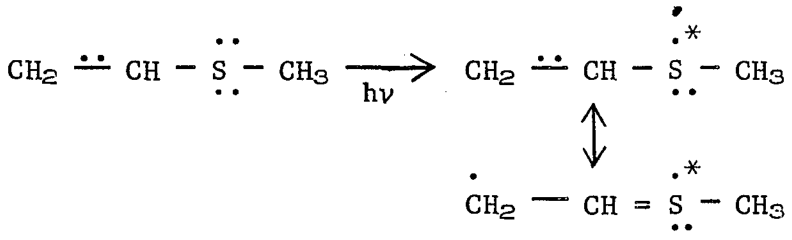
Compound	λ_{max}[a] A	ϵ
$(C_2H_3)_3B$	234	19,400
$(C_2H_3)_2BCH_3$	220	13,300
$(C_2H_3)B(CH_3)_2$	196	9,800

---

a) Spectra taken in gas phase.

Another group of compounds which is related to the present study is the vinyl sulfides (see Table XVIII). Price[28,29] has demonstrated that the absorption peaks of dimethyl sulfide [210 mμ (log ϵ = 3.01); 229 mμ (log ϵ = 2.14)] are bathochromically shifted by replacing one or both methyl groups with vinyls. He considers the excitation to involve a transition of one of the unshared electrons on sulfur to one of its available 3d-orbitals. When sulfur has an unsaturated substituent such as a vinyl group, the remaining unpaired electron in the sulfur 3p-orbital[*] can now form a double bond with one of the electrons in the adjacent 2p-orbital on carbon.

The excited state can be visualized with the two resonance forms shown.



$$CH_2 \overset{\cdot\cdot}{-} CH - \underset{\cdot\cdot}{\overset{\cdot\cdot}{S}} - CH_3 \xrightarrow[h\nu]{} CH_2 \overset{\cdot\cdot}{-} CH - \underset{\cdot\cdot}{\overset{\cdot^{*}}{S}} - CH_3 \longleftrightarrow \dot{C}H_2 - CH = \underset{\cdot\cdot}{\overset{\cdot^{*}}{S}} - CH_3$$

It is this delocalization of the unpaired electron of the excited state which is responsible for the lower energy of the excited state in the vinyl substituted compound. Divinyl sulfide absorbs at even a lower energy than methyl vinyl sulfide. In divinyl sulfide, the vinyl groups may assume a coplanar configuration. The unshared electron in the 3p-orbital on the excited sulfur atom can now be delocalized into both vinyl groups leading to a further lowering of the energy of the excited

---

[*] The author has designated the unshared electrons as occupying 3p-orbitals. However, it is more likely that these orbitals have some "s" character.

Table XVIII[28,29]

Ultraviolet Absorption Spectra of Organo Sulfides

Compound	λ_{max} mμ	log ε	Solvent
CH_3-S-CH_3	210, 219	3.01, 2.14	Ethanol
CH_3-S-C_2H_5	210, 229	3.25, 2.14	Ethanol
C_2H_3-S-CH_3	230, 240	4.20, 4.00	95% Ethanol
C_2H_3-S-C_2H_3	240, 255	3.9, 3.8	95% Ethanol (Dioxane)
C_6H_5-S-CH_3	254, 275	3.98, 3.15	Ethanol
C_6H_5-S-C_2H_5	210, 256, 270	3.94, 3.90, 3.40	Ethanol
C_6H_5-S-C_6H_5	231, 250, 274	3.81, 4.08, 3.75	Ethanol
C_6H_5-S-C_2H_5	247, 266	4.02, 4.00	Ethanol

state. On the other hand, diphenyl sulfide absorbs at almost the same energy as phenyl methyl sulfide. The lack of added stabilization by adding a second phenyl group was explained on the basis of steric effects. Diphenyl sulfide is not considered to be a coplanar molecule (crystalline p,p' dibromodiphenyl sulfide has been shown to be nonplanar).[30] Therefore, the second phenyl group is ineffective in increasing the stability of the excited state of diphenyl sulfide.

The spectral trends for vinyl sulfides are analogous with those reported for vinylboranes (increase in number of vinyl groups leads to a decrease in absorption energy). The trends observed for these planar molecules have been interpreted on the basis of conjugation between the vinyl groups. By comparison with the present study, the above mentioned results strongly suggest that in vinylarsines and phosphines there is no conjugation between vinyl groups in the excited or ground state. This lack of conjugation would be consistent with the lack of planarity in the tervalent compounds of arsenic and phosphorus. The bond angles measured for various alkylarsines and phosphines have been reported to vary from 90° to 96°.[31,32]

The data obtained in the present study are consistent with the type of charge-transfer mechanism described by Cullen and Hochstrasser[18] for the arylarsines. In this case an electron would be removed from the non-bonded orbital of the central atom and transferred to the empty π^* orbital on <u>one</u> of the vinyl groups. The small but usually noticeable blue shift in the absorption maxima, upon substitution of a hydroxylic solvent for isooctane, is analogous to the observation of Cullen and Hochstrasser.

In this type of charge-transfer excited state, dative π bonding between the negatively-charged vinyl group and a vacant d-orbital on the positively-charged central atom is now possible. This dative π bonding would serve to stabilize the charge-transfer state. Thus a decreasing tendency from P to As toward p_π-d_π bonding might explain the lower transition energies observed for the vinylphosphines relative to the corresponding arsines. Although there is no large body of evidence on the relative tendencies of third and fourth row elements toward d_π-p_π bonding, some recent studies have indicated that the Ge and As 4d-orbitals are weaker π-acceptors (toward p_π orbitals) than the Si and P 3d-orbitals respectively.[33]

In order for the d-orbitals on the central atom to stabilize the π* acceptor orbital two requirements must be met. First, both orbitals must have appropriate symmetry to insure overlap. Second, both orbitals must be of comparable energy in order to make the overlap effective. Effective overlap is predicted by comparing the symmetry of the phosphorus d_{xz} orbital with the vinyl π* orbital (see Figure III).

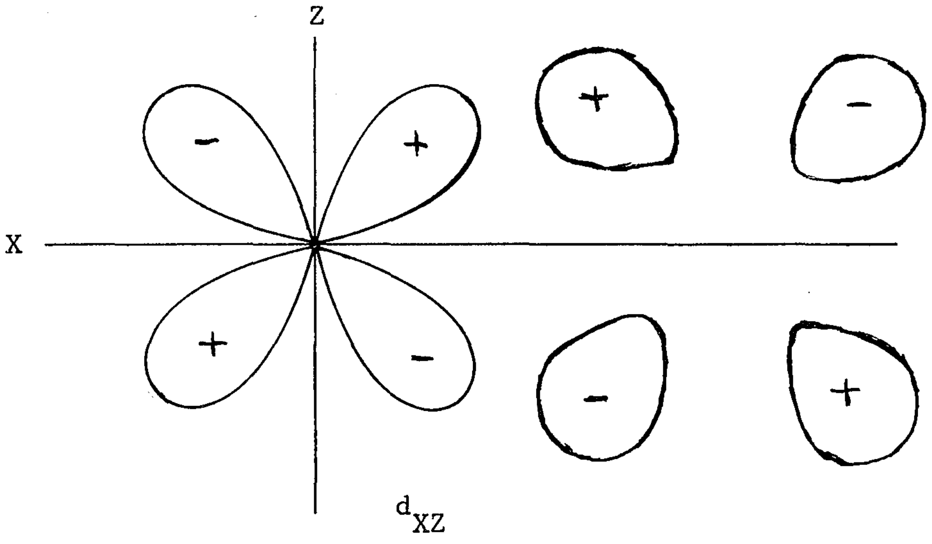


Figure III

Thus we have satisfied the first requirement.

Craig et al.[34,35] have reported calculations on the 3d-orbitals of phosphorus in compounds containing substituents capable of forming d_π-p_π bonds. Using Slater orbitals they found that when the phosphorus atom was neutral the 3d-orbitals were too diffuse (too high in energy) to permit d_π-p_π bonding. However, when the calculations were done for a positively charged phosphorus atom, the d-orbitals were contracted (lowered in energy) and resulted in an appreciable overlap. Therefore, it is not unreasonable to expect the phosphorus 3d-orbital to stabilize the excited π^* orbital of the vinyl group in a charge-transfer type transition.

EXPERIMENTAL DISCUSSION

Preparation of Vinylarsines

Due to the nature of the present study, it was essential to prepare several arsines, all of which had to be of high purity. Therefore, a synthetic route was sought which would satisfy two requirements. First, it must be useful in the preparation of a series of compounds. Second, each compound must meet certain criteria of purity. Although most of the compounds prepared had not been reported, a literature search provided some potentially useful routes. The purity of the compounds was unequivocally demonstrated by a combination of elemental analysis and nuclear magnetic resonance spectroscopy.

Maier[36] had reported that di-n-butyldivinyltin and arsenic tribromide undergo a redistribution reaction, producing a mixture of vinylbromoarsines. The resulting mixture of the two vinylbromoarsines could not be easily separated without the loss of a large intermediate fraction. It was therefore decided to prepare divinyliodoarsine and vinyldiiodorarsine, since it was believed that these two compounds could be separated more efficiently on account of the larger difference in molecular weights. These could then be treated with the various alkylmagnesium bromides to yield the desired compounds. Thus, the particular vinyliodoarsine could be prepared from tri-n-butylvinyltin and arsenic triiodide by adjusting the stiochiometry of the reactants:

(a) $2\ Bu_3SnVi + AsI_3 \rightarrow Vi_2AsI + 2\ Bu_3SnI$

(b) $Bu_3SnVi + AsI_3 \rightarrow ViAsI_2 + Bu_3SnI$

where Vi is vinyl.

The same experimental conditions were employed for reactions (a) and (b).

Divinyliodoarsine, from reaction (a), could be successfully isolated by distilling the entire reaction mixture and collecting the first fraction. The desired series of alkyldivinylarsines was then prepared from the single intermediate, divinyliodoarsine, and the corresponding alkylmagnesium halide (Table XIX).

In the preparation of vinyldiiodoarsine, the boiling point of the product continually fluctuated over a 20° range. It appeared that decomposition was occurring. This could be attributed to the presence of the high boiling tri-n-butyltin iodide. The solution of these two compounds could have necessitated a pot temperature which was high enough to cause decomposition of the arsine. An alternate method was suggested by the work of Maier,[36] who prepared a mixture of vinylbromoarsines via the following reaction:

$$\mathrm{Vi_3As + AsBr_3 \rightarrow Vi_2AsBr + ViAsBr_2}$$

It was therefore decided to treat the preformed divinyliodoarsine with arsenic triiodide:

$$\mathrm{Vi_2AsI + AsI_3 \rightarrow 2\ ViAsI_2}$$

The reaction was carried out under the same conditions used to prepare divinyliodoarsine. A deep red liquid, b.p. 85-86°/0.1 mm, was obtained which gave an elemental analysis corresponding to vinyldiiodoarsine. However, the compound darkened in color minutes after distillation. In addition, when it was treated with ethylmagnesium bromide or butylmagnesium bromide, mixtures of the dialkylvinylarsine and alkyldivinylarsine were obtained, as was shown by elemental analysis and nuclear magnetic resonance spectroscopy. The use of vinyldiiodoarsine was therefore abandoned. Thus the dialkylvinylarsines had to be prepared from the corresponding dialkylhaloarsines and either vinylmagnesium bromide or vinyllithium (Table XIX).

Dimethylvinylarsine was prepared from dimethyliodoarsine and vinyllithium. In the preparation of dimethyliodoarsine, commercially available dimethylarsinic acid (cacodylic acid) was reduced with sulfur dioxide in an acidic solution of potassium iodide, according to the procedure of van der Kelen.[37]

Diethylvinylarsine was prepared from diethylbromoarsine and vinylmagnesium bromide. The diethylbromoarsine was prepared by heating _in vacuo_ solid triethylarsine dibromide according to the method of Hartman.[38] The latter was obtained via the bromination of triethylarsine.

The reaction of trisodium arsinite with n-butyl bromide followed by reduction with sulfur dioxide in the presence of hydrobromic acid, yielded n-butyldibromoarsine.[39] This was converted to the sodium salt of n-butylarsonic acid which was then treated with n-butyl bromide to give di-n-butylarsinic acid after acidification. Reduction of the arsinic acid by the above mentioned procedure yielded di-n-butylbromoarsine. Di-n-butylbromoarsine was then obtained from the reaction between di-n-butylbromoarsine and vinylmagnesium bromide.

The preparation of heptafluoro-n-propyldivinylarsine was suggested by the work of Cullen,[40] who treated dimethyliodoarsine with trifluoromethyl iodide in the presence of mercury, and obtained dimethyltrifluoromethylarsine after constant stirring for five days. When divinyliodoarsine

Table XIX

Preparation of Vinylarsines

Substrate	Reactant	Product	% Yield	Ref.
$(CH_3)_2AsI$	C_2H_3Li	$C_2H_3As(CH_3)_2$	31	
$(C_2H_5)_2AsBr$	C_2H_3MgBr	$C_2H_3As(C_2H_5)_2$	53	
$(n\text{-}C_4H_9)_2AsBr$	C_2H_3MgBr	$C_2H_3As(n\text{-}C_4H_9)_2$	25	36
$(C_2H_3)_2AsI$	$C_3F_7I(Hg)$	$(C_2H_3)_2AsC_3F_7$	27	
$(C_2H_3)_2AsI$	CH_3MgBr	$(C_2H_3)_2AsCH_3$	59	
$(C_2H_3)_2AsI$	C_2H_5MgBr	$(C_2H_3)_2AsC_2H_5$	64	
$(C_2H_3)_2AsI$	$n\text{-}C_4H_9MgBr$	$(C_2H_3)_2As(n\text{-}C_4H_9)$	66	36
$C_6H_5AsCl_2$	C_2H_3MgBr	$(C_2H_3)_2AsC_6H_5$	53	
$AsBr_3$	C_2H_3MgBr	$(C_2H_3)_3As$	55	36

was treated with heptafluoro-n-propyl iodide in the presence of mercury, the reaction was complete after a few minutes of shaking and yielded heptafluoro-n-propyldivinylarsine. The product gave correct carbon, hydrogen and fluorine elemental analyses for $n\text{-}C_3F_7As(C_2H_3)_2$ and its nuclear magnetic resonance spectrum showed only vinylic hydrogens.

In all cases the nuclear magnetic resonance spectrum of the final product exhibited the correct ratio of alkyl to vinyl hydrogens. Moreover, it was found that a mixture of a dialkylvinylarsine and the corresponding alkyldivinylarsine could be detected by the appearance of more vinyl peaks than either of the two exhibited alone. None of the nuclear magnetic resonance spectra showed any regions of absorption other than the alkyl or vinyl.

Preparations of Vinylphosphines

As in the work on the arsines, it was essential to prepare pure samples of the various phosphines.

Ethyldichlorophosphine was prepared by the redistribution reaction of phosphorous trichloride with tetraethyllead. Maier[41] has shown that by adjusting the reaction temperature, one can easily control the number of ethyl groups substituted onto the phosphorus, so that ethyldichlorophosphine can be prepared free of the disubstituted compound. The sample of ethyldichlorophosphine prepared gave a correct chlorine analysis.

Diethylchlorophosphine was prepared via the known intermediate tetraethylbi(phosphine sulfide).[42] This compound was chlorinated with chlorine gas to give diethylchlorophosphine sulfide[43] and the latter was then desulfurized with tri-n-butylphosphine.[44] After desulfurization, diethylchlorophosphine was obtained as demonstrated by a correct chlorine elemental analysis and the lack of any chlorinated carbon atoms in the nuclear magnetic resonance spectrum.

Fox[45] reported the preparation of n-butyldichlorophosphine by the reaction of di-n-butylcadmium and phosphorus trichloride. Therefore, it was decided to prepare both n-butyldichlorophosphine and di-n-butylchlorophosphine with the use of di-n-butylcadmium. In the preparation of n-butyldichlorophosphine the molar ratio of phosphorus trichloride to di-n-butylcadmium was 3/1. This would minimize the formation of any di-n-butylchlorophosphine and tri-n-butylphosphine. The unreacted phosphorus trichloride, b.p. 71°/760 mm was easily distilled as a forecut from the n-butyldichlorophosphine, b.p. 56°/18 mm. Any small amounts of di-n-butylchlorophosphine and tri-n-butylphosphine remained in the distilling flask as a residue. The compound obtained gave a correct carbon and hydrogen elemental analysis for $C_4H_9PCl_2$.

Di-n-butylchlorophosphine was prepared by treating phosphorus trichloride and di-n-butylcadmium in a 1/1 molar ratio, with a 5% excess of phosphorus trichloride. The excess phosphorus trichloride was used as an attempt to limit the formation of tri-n-butylphosphine. The isolated compound gave a correct carbon and hydrogen elemental analysis for $(C_4H_9)_2PCl$.

There are reports in the literature[46,47,48] describing the preparation of vinylphosphines by the reaction of vinylmagnesium halide with either phosphorus trichloride or various alkylhalophosphines. The following reactions were attempted:

$$3ViMgBr + PCl_3 \rightarrow Vi_3P + 1.5\ MgBr_2 + 1.5\ MgCl_2$$

$$2ViMgBr + EtPCl_2 \rightarrow Vi_2PEt + MgBr_2 + MgCl_2$$

$$ViMgBr + Et_2PCl \rightarrow ViPEt_2 + .5\ MgBr_2 + .5\ MgCl_2$$

After hydrolysis of the Grignard reagent and removal of the ether, no volatile phosphorus containing compounds could be isolated. It has been reported[49] that the difficulty in isolating aliphatic phosphines formed via Grignard reagents is due to the formation of complexes between magnesium salts and the phosphine. This complex cannot be broken by acidic hydrolysis.

Isbell[50] has reported the alkylation of alkylhalophosphines with alkyllithium reagents, at low temperatures. Therefore, it was decided to try vinyllithium as the vinylating reagent (see Table XX). The vinylations were carried out at -78° in order to limit any possible side reactions. Reaction was noted to occur at this low temperature by an immediate white precipitate that formed on addition of vinyllithium to the chlorophosphine. It was found convenient, in the work-up of the product, to separate the ether solution from the formed insoluble lithium salts prior to hydrolysis. In this way the organic phase obtained after hydrolysis could be simply dried and distilled to yield the desired product.

As in the case of the arsines, each product gave a correct elemental analysis for carbon and hydrogen. In addition the nuclear magnetic resonance spectrum showed the correct ratio of alkyl to vinyl hydrogens and the absence of any extraneous hydrogens.

Table XX

Preparation of Vinylphosphines

Substrate	Reactant	Product	% Yield	Ref.
$(C_2H_5)_2PCl$	C_2H_3Li	$(C_2H_5)_2PC_2H_3$	43	46
$(n\text{-}C_4H_9)_2PCl$	C_2H_3Li	$(n\text{-}C_4H_9)_2PC_2H_3$	33	64
$C_2H_5PCl_2$	C_2H_3Li	$C_2H_5P(C_2H_3)_2$	45	47
$n\text{-}C_4H_9PCl_2$	C_2H_3Li	$n\text{-}C_4H_9P(C_2H_3)_2$	43	
$C_6H_5PCl_2$	C_2H_3Li	$C_6H_5P(C_2H_3)_2$	26	62
PCl_3	C_2H_3Li	$P(C_2H_3)_3$	60	46,47

Preparation of Oxides

Since the oxides of both the phosphines and arsines proved to be extremely hydroscopic, all possible precautions were taken to insure exclusion of water throughout the entire synthetic procedure. All glassware (including melting point tubes) were heated at 180° and allowed to cool in a dessicator before being used. All manipulations were carried out in a glove bag under a prepurified nitrogen atmosphere. Melting point tubes were filled under nitrogen and the open end sealed with vacuum stopcock grease before being used to record a melting point.

The following four compounds were oxidized: trivinylphosphine, di-n-butylvinylphosphine, diethylvinylphosphine and n-butyldivinylarsine.

Zingaro[51] recently reported the oxidation of several trialkylarsines with red mercuric oxide as the oxidizing agent and dry acetone as the solvent.

Although di-n-butylvinylphosphine was oxidized with mercuric oxide, manganese dioxide proved to be a superior oxidizing agent, especially for the arsines. Mercuric oxide oxidations required the use of high boiling polar solvents (dimethylformamide) and long reaction times. Under these conditions, the oxides had a tendency to decompose; with manganese dioxide, the reaction temperature could be kept below 50° (pentane or hexane could be used as solvent) and a twenty-four hour reaction time yielded sufficient product for the present study. The product was purified by first removing the solvent from the reaction mixture. Then the crude solid was recrystallized to remove any unreacted starting material. After recrystallization, it was sublimed _in vacuo_ and recrystallized a second time. A final sublimation yielded oxides which were shown to be pure by elemental analysis and nuclear magnetic resonance spectroscopy. The nuclear magnetic resonance spectrum showed the correct ratio of alkyl to vinyl hydrogens and did not exhibit any extraneous hydrogens.

The manganese dioxide was prepared as described by Attenburrow.[52] However, the oxide was heated for twenty-four hours at 120° instead of four hours as suggested by Attenburrow.

Experimental

Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, New York and Galbraith Laboratories Inc., P. O. Box 4187, Knoxville 21, Tennessee.

Melting points were taken on a Thomas Hoover Capillary melting point apparatus.

Nuclear magnetic resonance spectra were taken on a Varian A-60 spectrometer.

All reactions were run under an atmosphere of argon or prepurified nitrogen. The apparatus was alternatively evacuated and flushed with the inert gas several times.

The ether and tetrahydrofuran used were "anhydrous" reagent grade and were freshly distilled from lithium aluminum hydride before being used.

<u>Preparation of Starting Materials</u>. <u>Preparation of Tri-n-butylvinyltin.</u> -- Tri-n-butylvinyltin was prepared from bis(tri-n-butyl)tin oxide* and vinylmagnesium chloride according to the procedure of Rosenberg.[53] The product was distilled at 82°/0.3 mm. Reported,[53] b.p. 114°/3.0 mm.

---

*Obtained from Metal and Thermit Corporation, Rahway, New Jersey.

Preparation of Phenyllithium. -- Phenyllithium in diethyl ether was prepared from bromobenzene and lithium wire by the method of Ziegler.[54] The solution was standardized by hydrolysis of an aliquot, followed by titration of the formed lithium hydroxide with a standard solution of sulfuric acid.

Preparation of Vinyllithium. -- Vinyllithium was prepared by the reaction of phenyllithium and tetravinyltin in an ether solution, according to the method of Seyferth and Weiner.[55] The precipitated tetraphenyltin was allowed to settle to the bottom and an aliquot of the clear ethereal solution was titrated with a standard solution of sulfuric acid.

Preparation of Vinylmagnesium Bromide. -- Vinylmagnesium bromide was prepared by the reaction of vinyl bromide and magnesium in tetrahydrofuran, as described by Normant.[56] The concentration of an aliquot was determined by adding an excess of a standard sulfuric acid solution and then back-titrating the excess sulfuric acid with a sodium hydroxide solution of known concentration.

Preparation of Arsenic Triiodide. -- Arsenic triiodide was prepared by the method of Bailar.[59] It was sublimed at 100°/0.2 mm before being used.

Preparation of Divinyliodoarsine. -- A three-necked flask equipped with a magnetic stirring bar was charged with 381 g (1.2 moles) of tri-n-butylvinyltin. The flask was heated in an oil bath; when the temperature rose to 130°, 273 g (0.6 mole) of arsenic triiodide was added.

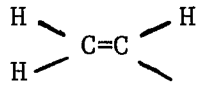
The heterogenous mixture formed a deep red solution when the temperature of the oil bath rose to 140°. The temperature was then maintained at 130° for twenty-four hours while the solution was stirred under nitrogen. After twenty-four hours, the solution appeared to be much lighter in color. The entire mixture was then distilled under a vacuum, and the lower boiling material (30-32°/0.2 mm) yielded 103 g (66%) of divinyliodoarsine after two distillations at 62°/7.5 mm. Reported,[36] b.p. 83°/17 mm. The nmr spectrum showed only vinylic hydrogens.

Anal. Calcd for C_4H_6AsI: C, 18.77; H, 2.37; I, 49.59. Found: C, 19.02; H, 2.52; I, 49.41.

Preparation of Vinyldiiodoarsine. -- Arsenic triiodide (112 g, 0.25 mole) was heated in a 500 ml round-bottom flask equipped with a magnetic stirrer. When the oil bath temperature rose to 120°, 63.3 g (0.25 mole) of divinyliodoarsine was added. After fifteen minutes at 120°, the heterogenous mixture formed a deep red solution. The temperature of the solution was maintained at 120-125° for three hours and then allowed to cool to room temperature. Upon cooling, a quantity of arsenic triiodide (identified by its melting point) precipitated out of solution. The mixture was stirred and heated for one more hour at 120° (a solution formed once more) and allowed to come to room temperature overnight. Arsenic triiodide again separated out of solution. The liquid was then decanted and distilled in vacuo. A forecut of 39.0 g of divinyliodoarsine, b.p. 35°/0.1 mm was followed by a 44.0 g fraction, b.p. 85-86°/0.1 mm. The latter was subsequently identified as vinyldiiodoarsine.

The divinyliodoarsine was poured back into the flask with the remaining arsenic triiode and stirred at 120° for seven hours. This reaction yielded an additional 22.5 g of vinyldiiodoarsine, b.p. 85-86°/0.1 mm. The nmr spectrum showed only vinylic hydrogens.

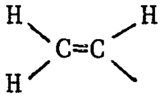
Anal. Calcd for $C_2H_3AsI_2$: I, 71.34. Found: I, 71.60.

Preparation of Perfluoro-n-propyldivinylarsine. -- In a glove bag filled with argon, a 250 ml round-bottom flask was charged with 30.0 g (0.10 mole) of heptafluoro-n-propyl iodide,* 9.0 g (0.035 mole) of divinyliodoarsine and 188 g of mercury. The stoppered flask was removed from the bag and cooled in a dry-ice acetone bath. After sufficient cooling, the flask was evacuated and then allowed to warm to room temperature. During this time, it was vigorously shaken by hand and it became noticeably warm. At this point, a green solid formed which obscured the other components of the mixture. Shaking was continued for fifteen minutes and a liquid which was lighter in color than the starting material began to separate from the green mass. When the flask had cooled to room temperature, the reaction appeared to be completed. The contents were then filtered in the glove bag, and the residue was washed twice with tetrahydrofuran. Removal of the tetrahydrofuran from the combined organic filtrates left a residue which upon two distillations yielded 2.3 g (27%) of perfluoro-n-propyldivinylarsine, b.p. 44°/40 mm. The nmr spectrum (neat) consisted of a multiplet at $\tau = 3.16\text{-}4.40$ ().

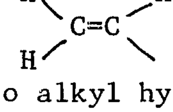
Anal. Calcd for $C_7H_6F_7As$: C, 28.21; H, 2.02; F, 44.61. Found: C, 28.44; H, 2.17; F, 44.45.

---

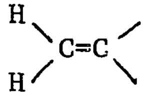
*Purchased from K & K Laboratories, Plainview, New York.

Preparation of Methyldivinylarsine. -- Freshly distilled divinyliodoarsine (31.8 g, 0.12 mole) in 40 ml of ether was added dropwise to 0.15 mole of methylmagnesium iodide in 200 ml of ether. The rate of addition was controlled to allow a gentle refluxing of the solvent. When the addition was complete, the reaction mixture was refluxed for one hour. A saturated ammonium chloride solution was then added to hydrolyze the unused Grignard reagent. Upon careful addition of the ammonium chloride solution, the magnesium salts form solid particles which are easily filtered. At this point, the ether is usually dry and requires no further treatment. However, some anhydrous magnesium sulfate was added to the mixture to insure dryness. The mixture was then filtered under nitrogen, and the ether was removed by distillation. The residue yielded, after two distillations, 10.0 g (59%) of methyldivinylarsine, b.p. 102°/760 mm. The nmr spectrum (CCl_4) consisted of a multiplet at τ 3.23-4.58 ( $H_2C{=}CH-$) and a singlet at τ 8.94 (CH_3). The ratio of vinyl to alkyl hydrogens was 2/1.

Anal. Calcd for C_5H_9As: C, 41.69; H, 6.29: Found: C, 41.94; H, 6.36.

Preparation of Ethyldivinylarsine. -- Freshly distilled divinyliodoarsine (49.0 g, 10.1 mole) in 50 ml of ether was added dropwise to 0.25 mole of ethylmagnesium bromide in 30 ml of ether. The product was treated as described above and yielded 19.4 g (64%) of ethyldivinylarsine, b.p. 54°/40 mm. The nmr spectrum (neat) consisted of a multiplet at τ 3.28-4.63 ( $H_2C{=}CH-$) and a multiplet at τ 8.27-9.13 (C_2H_5). The ratio of vinyl to alkyl hydrogens was 6/5.

Anal. Calcd for $C_6H_{11}As$: C, 45.59; H, 7.01: Found: C, 45.74; H, 7.07.

Preparation of n-Butyldivinylarsine. -- A solution of 0.11 mole of n-butylmagnesium bromide in 200 ml of ether was added dropwise to 13.3 g (0.05 mole) of freshly distilled divinyliodoarsine in 100 ml of ether. The product was worked-up as described above and yielded 6.0 g (66%) of n-butyldivinylarsine, b.p. 64°/18 mm. Reported[36] b.p. 56°/12 mm. The nmr spectrum (neat) consisted of a multiplet at τ 3.32-4.64 () and a multiplet at τ 8.5-9.3 (C_4H_9). The ratio of vinyl to alkyl hydrogens was 2/3.

Anal. Calcd for $C_8H_{15}As$: C, 51.62; H, 8.12. Found: C, 51.49; H, 8.10.

Preparation of Dimethyliodoarsine. -- Dimethyliodoarsine was prepared by the method of van der Kelen.[37] A solution containing 42.2 g (0.31 mole) of dimethylarsinic acid in 35 ml of water was combined with a solution of 50.0 g (0.31 mole) of potassium iodide in 40 ml of water. Enough dilute sulfuric acid was added to make the solution slightly acidic. The mixture was then transferred to a 250 ml, one-necked, round-bottom flask and sulfur dioxide was bubbled into the solution through a gas dispersion tube. Within one hour, a yellow oil appeared at the bottom of the flask. After the oil was removed, the aqueous portion was again saturated with sulfur dioxide. The mixture was stirred overnight and another quantity of product was obtained. The two oily products were dissolved in petroleum ether and the sulfur which accumulated during the reaction was filtered. The petroleum ether was removed, and after two distillations 50.7 g (70%) of dimethyliodoarsine, b.p. 53°/20 mm, was obtained. Reported,[37] b.p. 154-155°/760 mm.

Preparation of Diethylbromoarsine. -- Diethylbromoarsine was prepared according to the method of Hartman.[38] A weighed 250 ml, three-necked, round-bottom flask; fitted with a water condenser and a magnetic stirring bar was charged with 42.1 g (0.26 mole) of triethylarsine in 150 ml of carbon tetrachloride. A solution of 40.0 g (0.25 mole) of bromine in 15 ml of carbon tetrachloride was then added in one portion. The reaction mixture was stirred and the bromine color disappeared instantaneously. The solvent was removed *in vacuo* and 79.0 g (96%) of triethylarsine dibromide, m.p. 99-101°, remained in the flask. Reported,[38] m.p. 100°.

The flask was fitted with a distilling head and condenser for a downward distillation, and the apparatus evacuated to a pressure of 15 mm. The flask was then warmed in an oil bath and when the solid had completely melted (100°), a pale yellow liquid distilled. Upon redistillation, 36.3 g (68% based on Et_3AsBr_2) of diethylbromoarsine was obtained, b.p. 68°/15 mm. Reported,[38] b.p. 47°/5 mm.

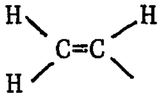
Anal. Calcd for $C_4H_{10}AsBr$: Br, 37.52. Found: Br, 37.60.

Preparation of n-Butylarsonic Acid.[39] -- A solution containing 198 g (1.0 mole) arsenic trioxide and 240 g (6.0 moles) of sodium hydroxide in 500 ml of water was placed in a two liter, three-necked flask equipped with a motor driven stirrer, reflux condenser and addition funnel. The stirred solution was cooled to room temperature and 272 g (2.0 moles) of n-butyl bromide in 30 ml of ethanol was added. After the addition was complete, the contents of the flask were refluxed by heating with an oil bath. The progress of the reaction was followed by titrating aliquots with standard iodine solution and determining the amount of unreacted arsenic(III) in solution. After eighty-four hours of refluxing the reaction mixture, all volatile organic materials were removed *in vacuo*. The remaining solution was made acidic to phenol phthalein and any unreacted arsenic trioxide was removed by filtration. Evaporation of the water left a syrup, which upon crystallization from ethanol, yielded 75.0 g (0.41 mole) of n-butylarsonic acid, m.p. 157-159°. Reported,[39] m.p. 159-160°.

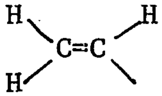
Preparation of n-Butyldibromoarsine. -- Concentrated hydrobromic acid was added to 75.0 g (0.41 mole) of n-butylarsonic acid until the latter was completely dissolved. A trace of potassium iodide was then added and the solution was saturated with sulfur dioxide according to the procedure of Banks.[39] The oil which separated out was dissolved in petroleum ether and the solution was filtered to remove traces of solid impurities. The filtrate yielded, after two distillations, 57.0 g (46%) of n-butyldibromoarsine, b.p. 65-67°/0.6 mm.

Preparation of Di-n-butylarsinic Acid.[39] -- A one liter, three-necked flask (equipped as in the preparation of n-butylarsonic acid) was charged with a solution containing 32.0 g (0.80 mole) of sodium hydroxide and 57.0 g (0.19 mole) of n-butyldibromoarsine in 70 ml of water. After the stirred solution was cooled to room temperature, 27.0 g (0.20 mole) of n-butyl bromide was added. When the addition was complete the reaction mixture was refluxed for six hours. Upon cooling, the solution was acidified to congo red paper, and all volatile organic residues were removed *in vacuo*. The di-n-butylarsinic acid was not isolated; instead the remaining crude syrup was used to prepare di-n-butylbromoarsine.

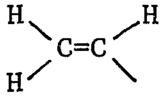
Preparation of Di-n-butylbromoarsine. -- Concentrated hydrobromic acid was added to the crude di-n-butylarsinic acid (vide supra) until the latter was completely dissolved. Following the addition of a trace of potassium iodide, reduction of the arsinic acid was carried out as described in the preparation of n-butyldibromoarsine. The petroleum ether extract yielded, after two distillations, 16.5 g (0.06 mole) of di-n-butylbromoarsine, b.p. 85-87°/3 mm. Reported,[36] b.p. 85-86°/2 mm.

Preparation of Dimethylvinylarsine. -- A 1.2 M ethereal solution of vinyllithium (0.2 mole) was prepared by the reaction between tri-n-butylvinyltin and n-butyllithium at -10°. To this was added dimethyliodoarsine (36.9 g, 0.16 mole) in 100 ml of ether. The rate of addition was adjusted to allow a gentle refluxing of the solvent. After the addition was complete, the reaction was refluxed for an additional hour. A saturated ammonium chloride solution was then added to hydrolyze the unused organolithium reagent. The aqueous layer was removed and the organic layer was dried with anhydrous magnesium sulfate. After removal of the ether from the organic layer, dimethylvinylarsine was isolated from the residue by distillation at atmospheric pressure. A redistillation yielded 6.5 g (31%) of dimethylvinylarsine, b.p. 79-80° at atmospheric pressure. The nmr spectrum (neat) consisted of a multiplet at τ 3.16-4.64 () and a singlet at τ 9.01 (CH_3). The ratio of vinyl to alkyl hydrogens was 1/2.

Anal. Calcd for C_4H_9As: C, 36.38; H, 6.87. Found: C, 36.57; H, 6.84.

Preparation of Diethylvinylarsine. -- Diethylbromoarsine (35.3 g, 0.16 mole) in 30 ml of tetrahydrofuran was added dropwise at room temperature to 0.19 mole of vinylmagnesium bromide in 300 ml of tetrahydrofuran. The product was worked-up as described in the preparation of methyldivinylarsine, and yielded 13.8 g (53%) of diethylvinylarsine, b.p. 58°/39 mm. The nmr spectrum (neat) consisted of a multiplet at τ 3.27-4.59 () and a multiplet at τ 8.31-9.10 (-C_2H_5). The ratio of vinyl to alkyl hydrogens was 3/10.

Anal. Calcd for $C_6H_{13}As$: C, 45.01; H, 8.19. Found: C, 45.27; H, 8.24.

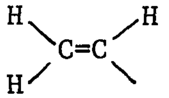
Preparation of Di-n-butylvinylarsine. -- Di-n-butylbromoarsine (16.5g, 0.06 mole) in 30 ml of tetrahydrofuran was added dropwise to 0.15 mole of vinylmagnesium bromide in 150 ml of tetrahydrofuran. The product was isolated as described above, and yielded 3.4 g (25%) of di-n-butylvinylarsine, b.p. 86-87°/10 mm. Reported,[36] b.p. 85-86°/10 mm. The nmr spectrum (CCl_4) consisted of a multiplet at τ 3.24-4.55 () and a multiplet at τ 8.5-9.3 (C_4H_9). The ratio of vinyl to alkyl hydrogens was 1/6.

Anal. Calcd for $C_{10}H_{21}As$: C, 55.55; H, 9.78. Found: C, 55.58; H, 9.68.

Preparation of Trivinylarsine. -- At room temperature, 47.0 g (0.15 mole) of arsenic tribromide* in 70 ml of tetrahydrofuran was added

---

*Purchased from K & K Laboratories, Plainview, New York.

dropwise to 0.5 mole of vinylmagnesium chloride in 200 ml of tetrahydrofuran. The product was treated as described above, and yielded 13.0 g (53%) of trivinylarsine, b.p. 49-50°/40 mm and 125° at atmospheric pressure. Reported,[36] b.p. 45-46°/41 mm. The nmr spectrum (neat) consisted of a multiplet at τ 3.33-4.64 ().

Anal. Calcd for C_6H_9As: C, 46.18; H, 5.81. Found: C, 46.32; H, 5.70.

Preparation of Phenyldivinylarsine. -- Vinylmagnesium bromide (100 ml, 0.09 mole) was added to a solution of 10.0 g (0.045 mole) of phenyldichloroarsine,* b.p. 126°/12 mm (reported b.p. 100-102/2mm)[58] in 40 ml of tetrahydrofuran. The rate of addition was controlled to allow a gentle refluxing of the solvent. After the usual work up, 5.2 g (55%) of phenyldivinylarsine, b.p. 44°/0.3 mm was obtained.

Anal. Calcd for $C_{10}H_{11}As$: C, 58.27; H, 5.37. Found: C, 58.41; H, 5.50.

Preparation of Thiophosphoryl Chloride.[59] -- A mixture of 507 g (3.7 moles) of phosphorus trichloride, 32.0 g (1.0 mole) of sulfur and 25.0 g of anhydrous aluminum chloride was warmed until the mixture started to bubble. At this point, external heating was stopped and a vigorous exothermic reaction ensued. The reaction was complete almost immediately as shown by the disappearance of the suspended sulfur. A 500 ml portion of water was then added to the reaction mixture in order

---

*Purchased from K & K Laboratories, Plainview, New York.

to dissolve the aluminum salts and two layers were formed. The lower layer (thiophosphoryl chloride) was separated, dissolved in diethyl ether and dried over anhydrous sodium sulfate. After filtering the drying agent and evaporating the ether, 507 g (95%) of thiophosphoryl chloride was obtained, b.p. 120° at atmospheric pressure. Reported,[59] b.p. 125-126° at atmospheric pressure.

Preparation of Tetraethylbi(phosphine sulfide).[42] -- A solution of 163 g (0.97 mole) of thiophosphoryl chloride in 500 ml of ether was added dropwise to 3.5 moles of ethylmagnesium bromide in 1.5 liters of ether. The reaction mixture was maintained at -50°. When the addition was completed the reaction mixture was hydrolyzed with a saturated ammonium chloride solution. Upon removal of the ether from the separated organic layer, a residue was obtained which when crystallized three times from ethyl alcohol yielded, 71.7 g (40%) of tetraethylbi(phosphine sulfide), m.p. 77-78°. Reported,[42] m.p. 75-76°.

Preparation of Diethylthiophosphinyl Chloride. -- Following the method described by Pollart,[43] 21.0 g (0.30 mole) of chlorine in 300 ml of carbon tetrachloride was added to 71.7 g (0.29 mole) of tetraethylbi(phosphine sulfide) in 400 ml of carbon tetrachloride. The addition was carried out slowly, and the contents of the flask were then stirred overnight. After removal of the solvent in vacuo, the residue yielded 79.4 g (85%) of diethylthiophosphinyl chloride, b.p. 88°/6 mm. Reported,[60] b.p. 60-61°/4 mm.

Preparation of Diethylchlorophosphine. -- According to the general procedure described by Maier,[44] a mixture of 79.4 g (0.50 mole) of diethylthiophosphinyl chloride and 105.g (0.52 mole) of tri-n-butylphosphine* was placed in a 300 ml one-necked, round-bottom flask. The flask was then attached to a vacuum jacketed vigreux column which was set-up for a downward distillation. The flask was heated in an oil bath at 180°. At a pressure of 50 mm, 40.0 g of a yellow liquid was collected, boiling between 51-60°. The distillate was redistilled twice and yielded 31.7 g (50%) of diethylchlorophosphine, b.p. 53°/50 mm. Reported,[61] b.p. 133-134°.

Anal. Calcd for $C_4H_{10}PCl$: Cl, 28.46. Found: Cl, 28.22.

Preparation of Ethyldichlorophosphine.[41] -- A mixture of 114 g (0.83 mole) of phosphorus trichloride and 100 g (0.31 mole) of tetraethyllead** were heated at 100° under a nitrogen atmosphere. At the end of twenty hours the precipitated ethyllead chlorides were allowed to settle out and the liquid was removed. The residue was then washed twice with 20 ml portions of petroleum ether, and all liquids were combined. After the petroleum ether was removed, two distillations of the remaining liquid yielded 45.8 g (42%) of ethyldichlorophosphine, b.p. 120° at atmospheric pressure. Reported,[45] b.p. 112° at atmospheric pressure. The nmr spectrum (neat) consisted of multiplet centered at τ 7.83 (CH_2) and a quintet centered at τ 8.76 (CH_3).

Anal. Calcd for $C_2H_5PCl_2$: Cl, 54.15. Found: Cl, 53.98.

---

*Purchased from the Metal and Thermit Caporation, Rahway, New Jersey.

**Sample obtained from the Ethyl Corporation.

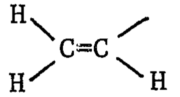
Preparation of Di-n-butylcadmium. -- The procedure of Fox[45] was employed in this preparation. A stirred solution containing 1.5 moles of butylmagnesium bromide in two liters of ether was cooled to -10° and 128 g (0.70 mole) of cadmium chloride (dried at 110°) was added in one portion. Stirring was continued for two more hours at -10°, and the salts were then allowed to separate to the bottom of the flask. The clear ethereal solution of di-n-butylcadmium was used immediately to prepare n-butyldichlorophosphine (*vide infra*).

Preparation of n-Butyldichlorophosphine. -- The above described cadmium reagent was added slowly to a stirred solution of 280 g (2.1 moles) of phosphorus trichloride in 400 ml of ether at -78°. After the addition was complete, the reaction mixture was allowed to come to room temperature and stirring was continued overnight. The cadmium salts were then allowed to settle to the bottom and the ethereal solution was decanted. The salts were washed with 300 ml of ether and both liquids were combined. The ether and unreacted phosphorus trichloride were distilled, leaving a residue which after two distillations yielded 90.0 g (81%) of n-butyldichlorophosphine, b.p. 56°/18 mm. Reported,[45] b.p. 58-60°/22 mm.

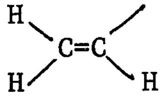
Anal. Calcd for $C_4H_9PCl_2$: C, 30.21; H, 5.70. Found: C, 29.92, H, 5.63.

Preparation of Di-n-butylchlorophosphine. -- To a stirred solution of 62.0 g (0.47 mole) of phosphorus trichloride in 500 ml of ether at -78°, was added 0.45 mole of di-n-butylcadmium in 1100 ml of ether. The addition was complete in about four hours, after which the reaction product was treated as previously described. Upon distillation, 8.0 g of a liquid, b.p. 68°/30 mm (presumably n-butyldichlorophosphine) was obtained as well as 46.0 g of a higher boiling fraction. Two distillations of the higher boiling material yielded 42.5 g (53%) of di-n-butylchlorophosphine b.p. 40°/0.5 mm. Reported,[63] b.p. 91-92°/12 mm; 77-81°/1 mm.

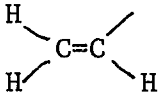
Anal. Calcd for $C_8H_{18}PCl$: C, 53.18; H 10.04. Found: C, 52.90; H, 10.07.

Preparation of Ethyldivinylphosphine. -- A three-necked flask equipped with a magnetic stirring bar and nitrogen inlet tube was charged with 10.6 g (0.08 mole) of ethyldichlorophosphine in 200 ml of ether. The solution was cooled to -78° and 0.16 mole of vinyllithium in 245 ml of ether was added dropwise. An immediate precipitate formed, which increased in amount as the addition was continued. Stirring was maintained after the addition was completed, and the contents of the flask were slowly warmed to room temperature. After one hour of additional stirring the lithium salts were allowed to settle to the bottom of the flask. The ethereal solution was transferred to another flask and subsequently hydrolyzed with a 1% sodium hydroxide solution. The aqueous layer was removed and the ethereal solution was dried with anhydrous magnesium sulfate. After filtering the drying agent under nitrogen the ether was removed by distillation. A liquid remained which yielded 4.1 g (45%) of ethyldivinylphosphine, b.p. 48°/54 mm; 121° at atmospheric pressure; reported[46] b.p. 121°/751 mm. The nmr spectrum (neat) consisted of a multiplet at τ 3.38-4.75 () and a multiplet at τ 8.23-9.28 ($-CH_2-CH_3$). The ratio of vinyl hydrogens to alkyl hydrogens was 6/5.

Anal. Calcd for $C_6H_{11}P$: C, 62.05; H, 11.28. Found: C, 61.88; H, 11.40.

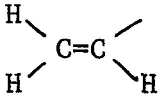
Preparation of Diethylvinylphosphine. -- A solution of 0.056 mole of vinyllithium in 100 ml of ether was added to 6.6 g (0.053 mole) of diethylchlorophosphine in 100 ml of ether. The reaction mixture was cooled to -78° during the addition process. The reaction mixture was treated as described above and yielded 2.7 g (43%) of diethylvinylphosphine, b.p. 48°/54 mm; 125° at atmospheric pressure. Reported[46] b.p. 125°/744 mm. The nmr spectrum (neat) consisted of a multiplet at τ 3.45-4.72 () and a multiplet at τ 8.25-9.29 (CH_2-CH_3). The ratio of vinyl hydrogens to alkyl hydrogens was 3/10.

Anal. Calcd for $C_6H_{13}P$: C, 63.14; H, 9.71. Found: C, 63.03; H, 9.80.

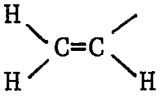
Preparation of n-Butyldivinylphosphine. -- A solution of 0.46 mole of vinyllithium in 730 ml of ether was added to 36.0 g (0.23 mole) of butyldichlorophosphine in 200 ml of ether at -78°. The reaction product was treated as described above and yielded 14.3 g (43%) of butyldivinylphosphine, b.p. 49-50°/11 mm. The nmr spectrum (neat) consisted of a multiplet at τ 3.59-4.90 (), a multiplet at τ 8.40-8.71 (CH_2-) and a multiplet at τ 8.91-9.20 (CH_3-). The ratio of vinyl hydrogens to alkyl hydrogens was 2/3.

Anal. Calcd for $C_8H_{15}P$: C, 67.58; H, 10.63. Found: C, 67.58; H, 10.42.

Preparation of Di-n-butylvinylphosphine. -- Following the usual procedure, 0.18 mole of vinyllithium in 220 ml of ether was added to 32.5 g (0.18 mole) of di-n-butylchlorophosphine in 200 ml of ether. The reaction yielded 10.3 g (33%) of di-n-butylvinylphosphine, b.p. 38°/0.7 mm.

Reported[64] b.p. 48-49°/2 mm. The nmr spectrum (neat) consisted of a multiplet at τ 3.63-4.98 (), a multiplet at τ 8.41 - 8.72 (CH_2-) and a multiplet at τ 8.92-9.23 (CH_3-). The ratio of vinyl hydrogens to alkyl hydrogens was 1/6.

<u>Anal</u>. Calcd for $C_{10}H_{21}P$: C, 69.73; H, 12.28. Found: C, 69.77; H, 12.33.

<u>Preparation of Trivinylphosphine</u>. -- Following the usual procedure, 0.16 mole of vinyllithium in 200 ml of ether was added to 7.0 g of phosphorus trichloride in 100 ml of ether. The reaction yielded 3.4 g (60%) of trivinylphosphine, b.p. 44°/50 mm. --Reported,[47] b.p. 58.1°/100 mm; 119°/760 mm.[46] The nmr spectrum (neat) consisted of a multiplet at τ 3.33-4.70 ().

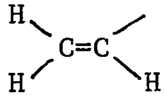
<u>Anal</u>. Calcd for C_6H_9P: C, 64.28; H, 8.09. Found: C, 64.44; H, 8.20.

<u>Preparation of Phenyldivinylphosphine</u>. -- Following the usual procedure, 0.23 mole of vinyllithium in 216 ml of ether was added to 20.3 g (0.11 mole) of phenyldichlorophosphine,[*] b.p. 68°/1 mm. (Reported[65] b.p. 99-101°/11 mm) in 200 ml of ether. The reaction yielded 4.7 g (26%) of phenyldivinylphosphine, b.p. 44°/0.4 mm. Reported,[62] b.p. 55°/0.5 mm.

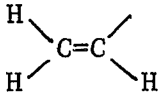
<u>Anal</u>. Calcd for $C_{10}H_{11}P$: C, 74.06; H, 6.83. Found: C, 73.96; H, 6.16.

---

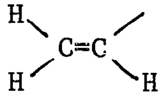
[*] Compound was purchased from K & K Laboratories, Plainview, New York 11803.

Preparation of Di-n-butylvinylphosphine Oxide. -- To a 250 ml three-necked flask, equipped with a nitrogen inlet tube and a magnetic stirring bar, was added 1.50 g (8.7×10^{-3} mole) of di-n-butylvinylphosphine, 30 ml of dimethylformamide (freshly distilled over anhydrous barium oxide) and 1.87 g (8.7×10^{-3} mole) of red mercuric oxide powder. After heating the contents of the flask in an oil bath at 45° for two days, the original red solid was decidedly dark grey. The contents of the flask were then filtered under a nitrogen atmosphere in a glove bag. Removal of the solvent from the filtrate *in vacuo*, left a green colored solid residue. Most of the green color was removed by crystallization of the solid from pentane. The crystallized solid was then sublimed at 55°/ 0.2 mm. and recrystallized from pentane. One final sublimation yielded, 0.30 g (19%) of white, crystalline, di-n-butylvinylphosphine oxide, m.p. 37-38°. Reported[64] m.p. 37.5-38°. The nmr spectrum ($CDCl_3$) consisted of a multiplet at τ 3.41-4.26 (), a multiplet at τ 7.70-8.85 (CH_2-) and a multiplet at τ 8.95-9.30 (CH_3-). The ratio of vinyl hydrogens to alkyl hydrogens was 1/6.

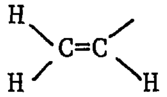
Anal. Calcd for $C_{10}H_{21}PO$: C, 63.81; H, 11.24. Found: C, 63.79; H, 11.18.

Preparation of Trivinylphosphine Oxide. -- To a 250 ml three-necked flask, equipped as described above, was added 1.04 g (9.2×10^{-3} mole) of trivinylphosphine, 50 ml of hexane and 2.5 g (2.8×10^{-2} mole) of manganese dioxide. This mixture was then heated in an oil bath at 50° . After twenty-four hours of heating the contents of the flask were filtered in a glove bag filled with nitrogen. The manganese dioxide was washed with 20 ml of tetrahydrofuran and both liquids were combined. Removal of the solvents in vacuo left a green solid. This was washed several times with pentane in order to remove any unreacted phosphine (trivinylphosphine oxide is insoluble in pentane). The solid was then crystallized from tetrahydrofuran and most of the green color was removed. Two sublimations at 80°/20 mm yielded 0.35 g (29%) of white, crystalline, trivinylphosphine oxide, m.p. 99-101°. The nmr spectrum ($CDCl_3$) consisted of a multiplet at τ 3.41-3.70 ().

Anal. Calcd for C_6H_9PO: C, 56.25; H, 7.08. Found: C, 55.77; H, 7.05.

Preparation of n-Butyldivinylarsine Oxide. -- In a flask fitted as described above, 1.40 g (7.5 x 10^{-3} mole) of n-butyldivinylarsine, 50 ml of spectroquality grade dioxane from a freshly opened bottle and 3.15 g (3.6 x 10^{-2} mole) of manganese dioxide were heated at 50° for twenty-four hours. Upon filtration and removal of the solvent, a brown solid material was obtained which was purified as described above. After the final sublimation at 60°/0.3 mm, 0.15 g (9%) of white, crystalline, n-butyldivinylarsine oxide, m.p. 66-67° was obtained. The nmr spectrum ($CDCl_3$) consisted of a multiplet at τ 3.41-3.70 (), a multiplet at τ 7.65-8.72 (CH_2-) and a multiplet at τ 8.85-9.21 (CH_3-). The ratio of vinyl hydrogens to alkyl hydrogens was 2/3.

Anal. Calcd for $C_8H_{15}AsO$: C, 47.54; H, 7.48. Found: C, 47.40; H, 7.27.

Preparation of Diethylvinylarsine Oxide. -- To a 250 ml three-necked flask, equipped as described above, was added 1.95 g (1.2×10^{-2} mole) of diethylvinylarsine, 50 ml of spectroquality grade dioxane from a freshly opened bottle and 4.1 g (4.7×10^{-2} mole) of manganese dioxide. The mixture was heated for twenty-four hours at 50°. The crude product was treated as outlined above. A final sublimation at 60°/0.3 mm, yielded 0.3 g (14%) of white, crystalline, diethylvinylarsine oxide, m.p. 95-96°. The nmr spectrum ($CDCl_3$) consisted of a multiplet at τ 3.38-3.71 (), a multiplet at τ 7.70-8.12 (CH_2-) and a multiplet at τ 8.51-8.89 (CH_3-). The ratio of vinyl hydrogens to alkyl hydrogens was 3/10.

Anal. Calcd for $C_6H_{13}AsO$: C, 40.93; H, 7.44. Found: C, 41.04; H, 7.50.

Ultraviolet Spectra. -- The ultraviolet spectra were obtained using a Cary Model 14 recording spectrophotometer. Solutions were prepared under an argon atmosphere in a glove bag. The sample was weighed in a 10.00 ± .02 ml volumetric flask and diluted to the mark. All solvents were spectral-grade (Matheson Coleman and Bell). The solution spectra were measured with a standard rectangular quartz cell fitted with a quartz insert to reduce the effective path length to 0.0649 mm. The path length was calibrated with a standard solution of potassium dichromate. All reported absorption coefficients are the average of three successive measurements with a minimum precision of ± 3%.

In order to obtain spectra in the gas phase, the compounds were transferred by expansion into an evacuated quartz cell of 10 mm path length, fitted with a stopcock and conical joint.

PART II

RESULTS AND DISCUSSION

In the last few years, some evidence has appeared in the literature which suggests the significance of d-orbital participation in the chemistry of organophosphines. Peterson[66] reported that alkyl tertiary phosphines were selectively metalated in the alpha position. Moreover, he found that a methyl group attached to a tertiary phosphorus atom was metalated more readily than a methyl group in an analogous amine. The apparent stabilization of a carbanion adjacent to a tervalent phosphorus atom was attributed to delocalization of the negative charge into an empty 3d-orbital on the central atom. Further evidence for this type of electron withdrawal was demonstrated by the isolation of Michael-type addition products resulting from the reaction of n-butyllithium with vinylphosphines.[67] The transition state of this reaction is believed to involve the formation of a negative charge on the carbon adjacent to the phosphorus atom. Kabachnik[68] has also discussed the Michael addition reactions of vinyl phosphorus compounds in terms of d-orbital participation.

As part of this investigation, evidence for the effectiveness of phosphorus in withdrawing an excess of electronic charge from adjacent atoms has been spectroscopically obtained. In the first part of this study, the observed maximum in the ultraviolet absorption spectra of vinylphosphines has been assigned to a charge-transfer type transition. This type of transition leads to an excess of negative charge on the vinyl group in the excited state. Therefore, if phosphorus is effective in partially withdrawing an excess of charge, substitution of a phosphorus atom for one of geminal hydrogens would result in a stabilization of the excited state. The compounds used in this study together with the relevant spectroscopic data appear in Table XXI.

From Table XXI, it is quite evident that substitution of a second tervalent phosphorus atom dramatically shifts the ultraviolet absorption maximum of vinylphosphines. The bathochromic effect can be explained by the delocalization of the optically excited electron into the empty 3d-orbitals on the second phosphorus atom. This interpretation is consistent with the work of Peterson[66,67] and Kabachnik.[68]

Oxidation of one of the phosphorus atoms produces an even greater bathochromic shift. The enhancement of the electron withdrawing power of phosphorus, when converted to a positively charge atom ($R_3\overset{+}{P}\text{-}\overset{-}{O}$), is expected. In addition, the monoxide exhibits a fairly large solvent effect which is absent in the vinylphosphines. This solvent effect is due to the hydrogen bonding of the negative oxygen atom to ethanol. Hydrogen bond formation enhances the electropositive character of phosphorus by retarding back bonding by the oxygen atom. Both of these observations clearly point out the ability of phosphorus to withdraw an excess of negative charge. Since the phosphorus atom in the monoxide is positively charged, the shift to longer wavelengths may in part be accounted for by an inductive effect. Unfortunately, this possibility is not excluded by this study. However, Schiemenz[14] has previously shown that the inductive effect of a pentavalent phosphorus atom on the ultraviolet absorption spectra of substituted phenylamines is not significant.

Table XXI

Ultraviolet Absorption Spectra of Bis(di-n-butylphosphines)[a]

Compound	Solvent[b]	λ_{max} mμ[c]	(ϵ_{max} x 10^3)
$(n\text{-}C_4H_9)_2P(C_2H_3)$	I	246	(2.60)
"	M	245	(2.63)
$(n\text{-}C_4H_9)_2PCH{=}CHP(n\text{-}C_4H_9)_2$	I	263	(4.18)[d] (2.75)[e]
"	M	263	(4.03)
$(n\text{-}C_4H_9)_2PCH{=}CHP(n\text{-}C_4H_9)_2$	I	263	(7.52)
"	M	263	(6.60)
$(n\text{-}C_4H_9)_2PCH{=}CHP(O)(n\text{-}C_4H_9)_2$	H	266	(6.14)
"	M	273	(5.15)
$(n\text{-}C_4H_9)_2(O)PCH{=}CHP(O)(n\text{-}C_4H_9)_2$	M	*ca*. 202-205[f]	
$(n\text{-}C_4H_9)_2P\text{-}P(n\text{-}C_4H_9)_2$	I	213, 240	(9.82), (7.16)
"	M	*ca*. 240[f]	
$(C_2H_5)_2As\text{-}As(C_2H_5)_2$	I	210,[g] 253	(14.8)
"	M	209,[g] 253	(12.9)

---

a) All compounds have the trans configurations except where indicated.

b) Isooctane (I), methanol (M), hexane (H).

c) Due to the broadness of the peak near the maximum, λ_{max} is reported only to the nearest mμ.

d) Reported ϵ_{max} for cis-trans mixture.

e) Calculated ϵ_{max} for pure cis compound (based on 70/30 mixture).

f) Region of inflection.

g) Appeared as shoulder on main peak.

EXPERIMENTAL DISCUSSION

Prior to this investigation there were no reports in the literature of any compounds of the type $R_2MCH=CHMR_2$ (where R is alkyl; M is As or P). The only disubstituted vinylene compound of this type that had been prepared was vinylenebis(diphenylphosphine). Aguiar[69] successfully prepared both cis- and trans-1,2-vinylenebis(diphenylphosphine) by the reaction of lithium diphenylphosphide (prepared in refluxing tetrahydrofuran) with the corresponding isomer of 1,2-dichloroethylene.

Although there are no other reported studies on the preparation of these vinylene compounds, the literature does contain two other articles which were particularly relevant to the present study. Issleib[70] found that the reaction of lithium dialkylphosphides in ether with $x\text{-}(CH_2)_n\text{-}x$ (where x is Cl or Br; n is 1,2) led to compounds of the type $R_2P\text{-}PR_2$. The reaction was thought to proceed via the following mechanism:

$$BrCH_2\text{-}CH_2Br + LiP(C_6H_{11})_2 \rightarrow BrCH_2\text{-}CH_2Li + (C_6H_{11})_2PBr$$

$$BrCH_2\text{-}CH_2Li \rightarrow H_2C=CH_2 + LiBr$$

$$(C_6H_{11})_2PBr + LiP(C_6H_{11})_2 \rightarrow (C_6H_{11})_2P\text{-}P(C_6H_{11})_2 + LiBr$$

However, Hewertson[71] succeeded in preparing 1,2-bis(diethylphosphino)-ethane $(C_2H_5)_2P\text{-}CH_2\text{-}CH_2\text{-}P(C_2H_5)_2$ by treating diethylchlorophosphine with lithium in tetrahydrofuran and adding 1,2-dichloroethane to the reaction mixture. In this case, the reaction favored the substitution product. From these studies, it appears that the solvent plays an important part in controlling the pathway of the reaction. This observation was crucial for the synthesis of the compounds needed for this study.

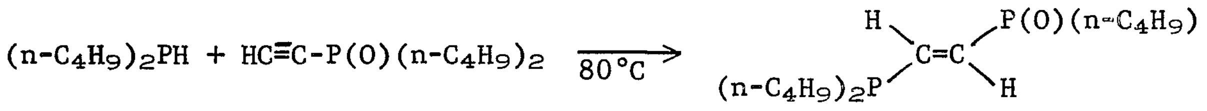
The first attempt to prepare trans-1,2-vinylenebis(di-n-butylphosphine) was via the room temperature addition of lithium di-n-butylphosphide (from phenyllithium and di-n-butylphosphine) to trans-1,2-dichloroethylene in ether. An nmr spectrum of the isolated product exhibited only alkyl and vinyl hydrogens in the ratio of 38/1. The correct ratio for the pure vinylene compound is 18/1. The deviation from the expected ratio of hydrogens together with the results of Isslieb suggested that the isolated product was a mixture of tetra-n-butylbiphosphine and trans-1,2-vinylenebis(di-n-butylphosphine). On the basis of this assumption, the nmr spectrum indicated that this mixture contained approximately equimolar amounts of the two compounds. Separation of the components of the mixture by fractional distillation failed to yield the pure product. An attempt to eliminate the formation of any biphosphine by using lower reaction temperatures was unsuccessful. It was therefore decided to run this reaction using tetrahydrofuran as the solvent. One drawback to this synthetic procedure was the instability of phenyllithium in tetrahydrofuran. This was avoided by preparing both the phenyllithium and the lithium di-n-butylphosphide in ether, and then replacing the solvent with tetrahydrofuran. Although the addition of tetrahydrofuran to the lithium reagent was highly exothermic, it does not appear that the lithium reagent was destroyed. This reaction led to the isolation of crude material in which the amount of desired product was far in excess of any tetra-n-butylbiphosphine. After several distillations of the crude material, the final product contained less than 1% of the biphosphine, as determined by gas liquid chromatographic analysis. No cis isomer was detected in a sample of the trans compound.

In the preparation of cis-1,2-vinylenebis(di-n-butylphosphine), the use of ether as the solvent led to the same results as described in the preparation of the corresponding trans isomer. Therefore, the reaction was carried out in tetrahydrofuran using the same procedure as described before. A gas liquid chromatographic analysis of the fractionally distilled product showed that it contained less than 1% of tetra-n-butylbiphosphine. However isomeric purity was not obtained in this case. At least 30% of the trans isomer was detected by gas liquid chromatographic analysis. It is quite possible that the initial product of the reaction was the cis isomer, which partially rearranged to the more thermodynamically stable trans isomer. This rearrangement could have occurred during the course of the reaction or during the purification of the product. Rearrangement of this type has been observed in other vinylmetallic systems.[72]

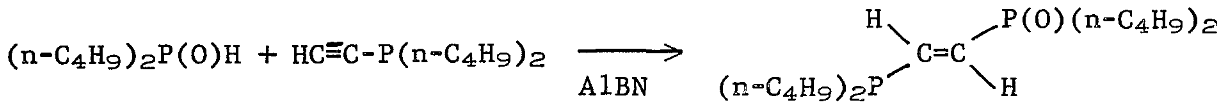
Lithium diethylarsenide was added to trans-1,2-dichloroethylene in tetrahydrofuran following the previously outlined reaction procedure. The only product obtained was tetraethylbiarsine. No further attempt was made to prepare 1,2-vinylenebis(dialkylarsines).

To complete this study, attempts were made to prepare the compounds $(n\text{-}C_4H_9)_2P(O)CH{=}CHP(n\text{-}C_4H_9)_2$ and $[(n\text{-}C_4H_9)_2\overset{+}{P}(CH_3)CH{=}CHP(n\text{-}C_4H_9)_2]X^-$.

Trans-1,2-vinylenebis(di-n-butylphosphine)monoxide is an unusual compound, for it contains both a tervalent phosphorus atom and a pentavalent (P-O) atom in the same molecule. It is understandable that no compounds of this type appear in the literature, since there are no known methods of oxidizing one tervalent phosphorus atom in the presence of another. Therefore, a synthetic route was sought which would lead directly to the monoxide. Two reactions were employed, both of which led to the isolation of the trans isomer:

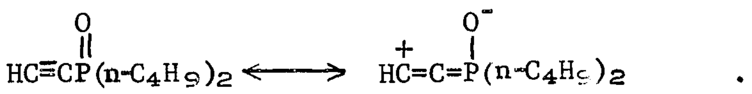


Reaction A



Reaction B

Reaction (A) is the first reported example of the addition of a secondary alkylphosphine across a triple bond in the absence of a free radical initiator. Since no initiator is required, it therefore appears possible that this addition takes place via a nucleophilic attack by the secondary phosphorus atom on the terminal carbon of the triple bond. This mechanism is reasonable when one considers the two possible resonance forms of the ethynylphosphine oxide:



$$HC{\equiv}C\overset{O}{\overset{\|}{P}}(n\text{-}C_4H_9)_2 \longleftrightarrow H\overset{+}{C}{=}C{=}\overset{O^-}{\overset{|}{P}}(n\text{-}C_4H_9)_2 \quad .$$

The partial positive charge on the terminal carbon atom would make it susceptible to a nucleophilic attack.

Reaction (B) is the first reported addition of a dialkylphosphine oxide across a triple bond. However, it has been reported that compounds such as R_2PH and $(RO)_2P(O)H$ react with compounds containing a double or triple bond in the presence of a free radical catalyst.[73] It is quite possible that the addition of a P-H bond across an unsaturated linkage is a general reaction.

The yields were rather low for reactions (A) and (B). This was due to the large amount of tarry material formed. Isolation of the product was made possible only by sublimation of the monoxide directly from the reaction flask. The crude sublimate contained unreated phosphine oxides which cosublimed. These impurities were removed with some difficulty by careful control of the temperature during sublimation. The purified compounds[*] isolated from reactions (A) and (B) had the same melting points (a mixed melting point showed no depression), and the nmr spectra of the two were identical.

The monoxide underwent a quaternization reaction with an excess of methyl iodide. After one crystallization of the crude product, 83% of a white crystalline solid was obtained which was shown by elemental analysis to be the 1:1 adduct. Since the reaction between trans-1,2-vinylenebis(di-n-butylphosphine) and methyl iodide yielded the 1:2 adduct as the only isolable product (_vide infra_), the presence of _one_ tervalent phosphorus atom in the monoxide is demonstrated. A similar result was obtained upon quaternization with methyl bromide.

Treatment of the products obtained from reactions (A) and (B) with hydrogen peroxide led to identical oxidation products. In each case, nearly quantitative yields were obtained, and the products had identical

---

[*] A correct carbon, hydrogen and phosphorus elemental analysis was obtained for both compounds.

nmr spectra and melting points. Moreover, the nmr spectra and melting points were identical with a sample of trans-1,2-vinylenebis(di-n-butylphosphine) dioxide which was prepared by the oxidation of trans-1,2-vinylenebis(di-n-butylphosphine) with hydrogen peroxide. This latter point provides substantial evidence that the monoxide has exclusively the trans configuration.

The nuclear magnetic resonance spectrum of pure trans-1,2-vinylenebis(di-n-butylphosphine) monoxide should theoretically exhibit a maximum of sixteen peaks in the vinyl region (see Figure IV).

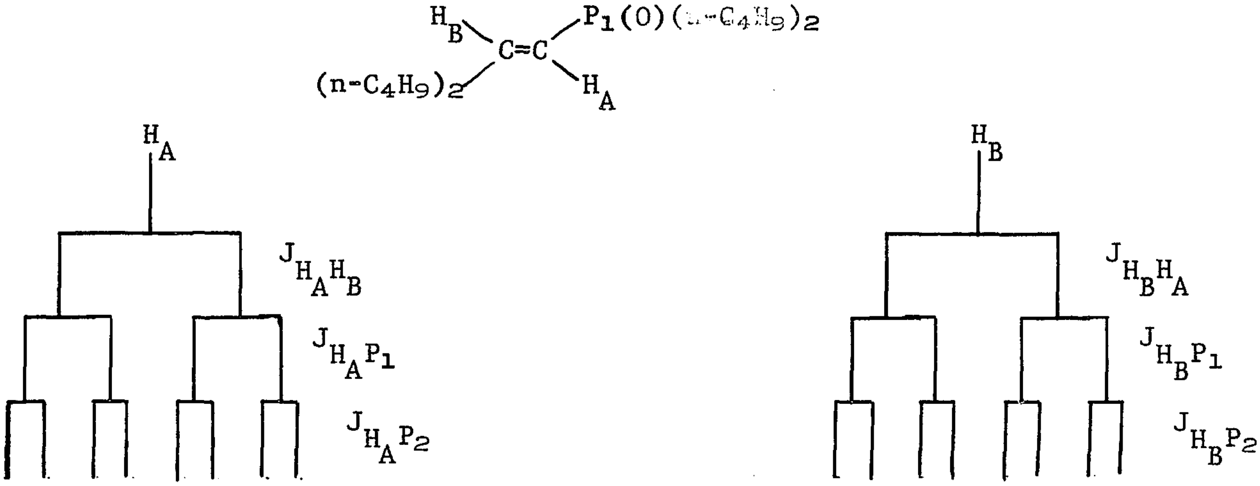
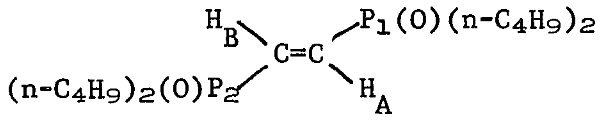


Figure IV

Oxidation of the monoxide would lead to a more symmetrical molecule and less coupling would be observed (see Figure V).



$H_A = H_B$

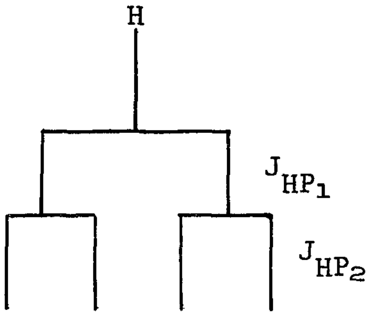


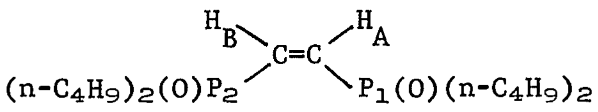
Figure V

In the dioxide, H_A is magnetically equivalent to H_B, and therefore no coupling is observed between these two hydrogens. Since geminal and vicinal coupling constants are different ($J_{HP_1} \neq J_{HP_2}$), the maximum number of peaks expected for this compound is four.

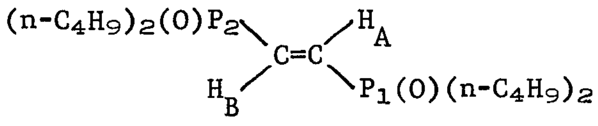
The monoxide spectrum appeared to consist of sixteen peaks in the vinyl region which is consistent with the above discussion. However, the dioxide appeared as two overlapping doublets. This is expected if $J_{HP_1} \cong J_{HP_2}$, leading to the overlap of the two central lines shown in Figure V. If either sample were contaminated with some of the cis isomer, the vinyl region would have been much more complicated. Additional peaks would be caused by the different J_{HP} couplings[*] (see Figure VI).

---

[*] Additional peaks were clearly observed for the cis- and trans-1,2-vinylenebis(di-n-butylphosphine) mixture.



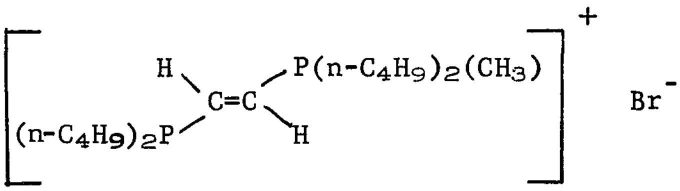
A



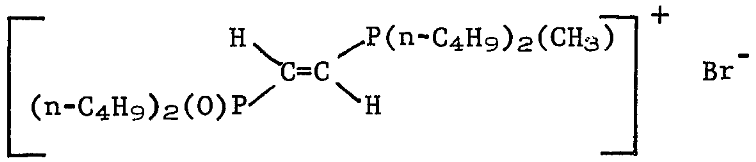
B

Figure VI

Two synthetic procedures were attempted for the preparation of di-n-butylmethyl(trans-β-di-n-butylphosphino)vinylphosphonium bromide:



The first method was suggested by the work of Fritzsche[74] who demonstrated the utility of reducing phosphine oxides with phenylsilanes and with trichlorosilane. The reported yields are quite good and isolation of the products did not appear difficult. Therefore, it was expected that treatment of the intermediate di-n-butylmethyl(trans-β-di-n-butylphosphinoxy)vinylphosphonium bromide (vide supra)



with either trichlorosilane or phenylsilane would lead to the desired compound. However, the reaction with either of the silanes led to the isolation of a solid which no longer contained a double bond. An infrared spectrum of the reaction product provided evidence that the silane had not only reduced the P-O group but also possibly added across the double bond. Since there was no apparent method to control the simultaneous reactions, this procedure was abandoned.

The second attempt to prepare the vinylphosphonium bromide was by direct quaternization of trans-1,2-vinylenebis(di-n-butylphosphine). This method was tried even though the literature contains many examples[70,75] where di-tertiary phosphines react with alkyl halides to produce only 1:2 adducts. Several alkyl halides were treated with trans-1,2-vinylenebis-(di-n-butylphosphine), but in each case only a 1:2 adduct was isolated.

EXPERIMENTAL

Preparation of Crude Tetra-n-butylbi(phosphine sulfide).[42] -- An ethereal solution of n-butylmagnesium bromide (8.0 moles) was prepared in a five liter, three-necked, round-bottom flask equipped with a mechanical stirrer. To this was slowly added a solution of 296 g (1.75 moles) of thiophosphoryl chloride in 400 ml of ether. The addition was carried out at 0° by cooling the flask in an ice-water bath. After the addition was completed, stirring was continued until the reactants in the flask had warmed to room temperature. The contents of the flask were then poured into a mixture of ice and a 10% sulfuric acid solution. The aqueous layer was separated from the organic layer and washed twice with 300 ml portions of ether. The ethereal solutions were combined and dried over anhydrous magnesium sulfate. The solution was then concentrated to a volume of 300 ml and subsequently used to prepare di-n-butylphosphine.

Preparation of Di-n-butylphosphine.[76] -- The ethereal solution of tetra-n-butyl(biphosphine), prepared as described in the preceding section, was added very slowly under nitrogen to a suspension of 50.0 g of lithium aluminum hydride (1.3 moles) in 300 ml of freshly distilled ether. After the addition was completed, the contents of the flask were warmed for thirty minutes in a hot water bath to allow gentle refluxing of the ether. The reaction mixture was then cooled in an ice-water bath, and distilled water was cautiously added. Hydrolysis was continued until the aluminum hydroxide formed fine solid particles which settled to the bottom of the flask. Some anhydrous sodium sulfate was added to the mixture to insure dryness. The flask was allowed to stand overnight and the ether was then decanted into a 500 ml, round-bottom distilling flask. After the solvent was removed by distillation under a nitrogen atmosphere, the residue was distilled at 0.05 mm and all materials boiling under 40° were collected. This fraction was then redistilled under a nitrogen atmosphere and yielded 93.0 g (35%) of di-n-butylphosphine, b.p. 182°. Reported,[75] b.p. 184-186°/760 mm.

Preparation of Lithium Di-n-butylphosphide. -- The preparation of the lithium phosphide reagent was carried out in accordance with the procedure outlined by Issleib for the preparation of lithium diethylphosphide.[77] An ethereal solution of phenyllithium (0.08 mole) contained in 76 ml of solvent was pipetted into a 250 ml, three-necked, round-bottomed flask, equipped with a magnetic stirrer. To this was slowly added a solution of 12.7 g (0.087 mole) of di-n-butylphosphine in 30 ml of freshly distilled ether. The slightly exothermic reaction was carried out under a nitrogen atmosphere. As soon as the addition was completed, the resulting solution of lithium di-n-butylphosphide was ready for further use.

Preparation of Tetra-n-butylbiphosphine. -- The method used by Issleib[70] to prepare tetraethylbiphosphine was adapted to the following procedure. After the above described lithium di-n-butylphosphide solution (0.08 mole) was cooled to 0° with an ice-water bath, 7.7 g (0.041 mole) of 1,2-dibromoethane was slowly added. Stirring was maintained throughout the addition and continued until the contents of the flask reached room temperature. Any remaining active lithium compounds were then hydrolyzed with water. The aqueous layer was removed from the flask, and the ether solution was dried overnight with anhydrous sodium sulfate.

The solution was then decanted and the ether distilled under nitrogen. The liquid residue was distilled using a 300 x 13 mm distilling column packed with 3/16" glass helices and heated with a circularly wound nichrome wire. At 0.1 mm, 2.0 g of a colorless liquid, b.p. 40-80°, was collected. A second fraction weighing 8.5 g was collected at 115-130°/0.02 mm. After two more distillations of the latter fraction, 5.0 g (40%) of tetra-n-butylbiphosphine, b.p. 98-100°/0.05 mm* was obtained. Reported,[78] b.p. 180-181°/14 mm. The nmr spectrum (neat) showed only alkyl hydrogens.

Anal. Calcd for $C_{16}H_{36}P_2$: C, 66.17; H, 12.49. Found: C, 66.06; H, 12.29.

Preparation of Trans-1,2-vinylenebis(di-n-butylphosphine).

Method A. Ether as Solvent. -- A solution containing 0.04 mole of lithium di-n-butylphosphide in 100 ml of ether was prepared as previously described. This was added at room temperature to a solution of 1.92 g (0.02 mole) of trans-1,2-dichloroethylene in 100 ml of ether. The addition was carried out at a rate sufficient to allow gentle refluxing of the solvent. After the addition was completed, the reaction mixture was hydrolyzed with enough saturated ammonium chloride solution to form two layers. The ethereal layer was then separated and dried with anhydrous sodium sulfate. After the ether was removed, two fractions were collected. The lower boiling fraction consisted of 0.50 g of a colorless liquid, b.p. 40-50°/0.3 mm. The higher boiling fraction was redistilled and 2.41 g of material was collected at 124-128°/0.15 mm. An nmr spectrum (neat) of

---

*The column was overheated during the first distillation of the biphosphine compound.

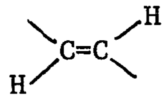
this material exhibited only alkyl and vinyl hydrogens in the ratio of 38/1 (correct ratio for pure product is 18/1). Two redistillations failed to yield the purified compound.

The same reaction was attempted at -78° using 0.034 mole of lithium di-n-butylphosphide and 0.017 mole of trans-1,2-dichloroethylene. After adding approximately 1/8 of the total volume of the lithium reagent, it appeared that no reaction had taken place. This conclusion was based on the persistence of the yellow color of the lithium phosphide solution, and the lack of any lithium chloride precipitation. The resulting reaction mixture was then allowed to warm slowly until there were signs of a reaction. At 0° the yellow color started to disappear. The reaction mixture was then maintained at temperatures between 0° and -10°, and the addition was completed. Stirring was then continued until the contents of the flask warmed to room temperature. The reaction products were isolated in the usual manner. Two fractions were collected. The first fraction consisted of 1.5 g of a liquid, b.p. 70-90°/0.5 mm, and the second fraction consisted of 1.5 g of a liquid, b.p. 132-142°/0.5 mm. An nmr spectrum (neat) of the second fraction was identical with that of the previously described preparation.

Preparation of Trans-1,2-vinylenebis(di-n-butylphosphine).

Method B. Tetrahydrofuran as Solvent. -- An ethereal solution of lithium di-n-butylphosphide was prepared as described above from 59.0 g (0.40 mole) of di-n-butylphosphine in 50 ml of ether and 0.38 mole of a 0.97 M solution of phenyllithium. The reaction flask was fitted with a distilling column and all but approximately 20 ml of ether was distilled off.

Most of the lithium di-n-butylphosphide separated out of solution and appeared as a yellow solid. The distilling apparatus was removed, and a 50 ml portion of tetrahydrofuran was then poured into the flask. The lithium salt quickly dissolved in the solvent accompanied by the liberation of heat. Most of the solvent was then quickly removed *in vacuo*, and another 50 ml portion of tetrahydrofuran was added. This time the contents of the flask were evaporated to dryness. The flask was then placed in an ice-water bath, and the solid lithium salt was dissolved in 100 ml of freshly distilled tetrahydrofuran. The solution was transferred to an addition funnel which was attached to a one liter, three-necked, round bottomed flask, equipped with a magnetic stirrer. The flask was charged with 200 ml of freshly distilled tetrahydrofuran and 18.6 g (0.19 mole) of trans-1,2-dichloroethylene. The dichloroethylene solution was cooled to -78°, and the lithium di-n-butylphosphide solution was added dropwise. The yellow color of the lithium reagent was immediately discharged, and a white solid separated from the solution. Stirring was maintained after the addition was completed, and the contents of the flask were slowly warmed to 0°. Upon completion of the reaction, enough distilled water was added to cause the formation of an aqueous layer. This was then removed and anhydrous sodium sulfate was added to the tetrahydrofuran solution. The dried solution was then decanted and the solvent was distilled off. The residue was distilled and the distillate consisted of 40.0 g of a colorless liquid, b.p. 100-130°/0.02 mm. This was redistilled using a 300 x 13 mm distilling column packed with 3/16" glass helices and heated with a circularly wound nichrome wire. Two fractions were collected. The first fraction weighed 20.0 g and distilled between 60-104°/0.05 mm. From this first fraction, 7.0 g of di-n-butylphosphine was recovered.

The second fraction, weighing 19.2 g, had a b.p. of 104-130°/0.05 mm. This second fraction was redistilled two more times to yield 15.0 g (23%) of trans-1,2-bis(di-n-butylphosphino)ethylene, b.p. 123-125°/0.05 mm. The nmr spectrum (neat) consisted of a multiplet at τ 3.38-3.73 (), a multiplet at τ 8.33-8.81 (-CH_2-) and a multiplet at τ 8.90-9.30 (CH_3-). The ratio of alkyl hydrogens to vinyl hydrogens was 18/1. A g.l.c. analysis of the isolated product showed that there was no cis-1,2-bis(di-n-butylphosphino)ethylene and less than 1% of tetra-n-butylbiphosphine present.*

Anal. Calcd for $C_{18}H_{38}P_2$: C, 68.31; H, 12.10. Found: C, 68.49; H, 12.20.

Preparation of Cis-1,2-vinylenebis(di-n-butylphosphine).

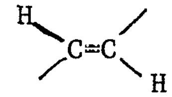
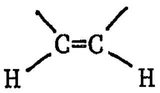
Method A. Ether as Solvent. -- A solution containing 0.039 mole of lithium di-n-butylphosphide in 100 ml of ether was prepared as previously described. A portion of this reagent was added to a cooled solution (-78°) of 1.89 g (0.018 mole) of cis-1,2-dichloroethylene in 100 ml of ether. After several minutes of stirring, the yellow color of the lithium reagent remained, and no solid lithium chloride was observed. Since there was no evidence of a reaction, the contents of the flask were slowly warmed. At 0°, the yellow color disappeared. The dichloroethylene solution was then maintained at temperatures between 0° and -10°, and the addition was completed. The contents of the flask were then heated as described in the preparation of the trans isomer. The reaction yielded 1.2 g of a liquid,

---

*Chromatography was carried out on a 6' x 1/8", 3% JXR Chrome Q, 100-120 mesh column using a Perkin-Elmer Model 881 gas chromatograph with a flame ionization detector.

b.p. 96-102°/0.3 mm and a second fraction weighing 2.6 g, b.p. 130-140°/0.4 mm. The nmr spectrum (neat) of the latter fraction exhibited only alkyl and vinyl hydrogens in a ratio of 38/1. No further purification of the material was attempted.

Preparation of Cis-1,2-vinylenebis(di-n-butylphosphine).

Method B. Tetrahydrofuran as Solvent. -- A solution of lithium di-n-butylphosphide was prepared as previously described from 27.0 g (0.18 mole) of di-n-butylphosphine and 0.17 mole of a 1.1 M solution of phenyllithium. This reagent was slowly added to a stirred solution of 8.0 g (0.083 mole) of cis-1,2-dichloroethylene in 100 ml of tetrahydrofuran at 0°. Isolation of the crude reaction product was carried out following the same procedure described for the corresponding trans compound. After removal of the solvent, 17.0 g of a colorless liquid, b.p. 80-130°/0.05 mm, was collected in a preliminary distillation. The crude distillate was then fractionated using the previously described distilling column. A substantial forecut, weighing 10.5 g, distilled at 60-106°/0.05 mm. The remaining liquid was collected in three fractions: a 1.5 g fraction, b.p. 106-112°/0.05 mm, a 3.0 g fraction, b.p. 114-118°/0.05 mm and a 1.7 g fraction, b.p. 118-120°/0.05 mm. A redistillation of the second fraction yielded 2.2 g of a liquid, b.p. 117-119°/0.05 mm whose nmr spectrum (neat) consisted of a multiplet at τ 3.38-3.82 ( and ), a multiplet at τ 8.48-8.82 ($-CH_2-$) and a multiplet at τ 9.10-9.52 (CH_3-). The ratio of alkyl to vinyl hydrogens was 18/1. A g.l.c. analysis of this product showed that it contained 30% of trans-1,2-vinylenebis(di-n-butylphosphine) and less than 1% of tetra-n-butylphosphine.

Anal. Calcd for $C_{18}H_{38}P_2$: C, 68.31; H, 12.10. Found: C, 68.26; H, 12.04.

The nmr spectrum of the third fraction showed that it contained a greater percentage of the trans isomer. Since the boiling points of these two isomers appear to be very close, no further separation was attempted.

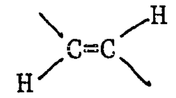
Preparation of Mono-ethynylmagnesium Bromide.[79] -- Ethylmagnesium bromide (0.25 mole) was prepared by treating 6.0 g (0.25 mole) of magnesium with 28.0 g (0.25 mole) of ethyl bromide in 200 ml of tetrahydrofuran. This reagent was then transferred to an addition funnel which was attached to a one liter, three-necked, round-bottom flask, containing 300 ml of dry tetrahydrofuran. Acetylene was bubbled into the solvent through a gas-dispersion tube for approximately five minutes. The Grignard reagent was then added to this stirred solution in 5-10 ml portions while a continuous stream of acetylene was maintained throughout the course of the reaction. No noticeable amount of heat was evolved during the reaction. After all the ethylmagnesium bromide had been added, the flow of acetylene was stopped, and the reagent was used immediately to prepare di-n-butylethynylphosphine.

Preparation of Di-n-butylethynylphosphine.[79] -- To a cooled solution (-20°) of 0.25 mole of ethynylmagnesium bromide in 300 ml of tetrahydrofuran was added 38.0 g (0.21 mole) if di-n-butylchlorophosphine. After the addition was complete, the reaction mixture was allowed to warm to room temperature. It was then hydrolyzed with a saturated ammonium chloride solution. The aqueous layer was removed and the organic layer was dried with anhydrous sodium sulfate. After removal of the solvent, a dark brown liquid remained which yielded upon distillation 20.0 g (59%) of di-n-butylethynylphosphine, b.p. 40°/0.4 mm. Reported,[79] b.p. 37/0.3 mm. The nmr spectrum (neat) consisted of a singlet at τ 7.28 (H-C≡), a multiplet at τ 8.25-8.72 ($-CH_2-$) and a multiplet at τ 8.90-9.25 (CH_3-). The ratio of alkyl to ethynyl hydrogens was 18/1.

<u>Preparation of Di-n-butylethynylphosphine Oxide</u>.[80] -- To a solution of 14.0 g (0.082 mole) of di-n-butylethynylphosphine in 30 ml of acetone was added in small portions 18.0 g (0.16 mole) of a solution of 30% hydrogen peroxide in 20 ml of acetone. The exothermic reaction was cooled occasionally with an ice-water bath. After the addition had been completed, the water and acetone were removed *in vacuo*. The oily residue was then sublimed at 50°/0.05 mm to yield 14.5 g (95%) of di-n-butylethynylphosphine oxide, m.p. 56-58°. Reported,[80] m.p. 55-58°. The nmr spectrum ($CDCl_3$) exhibited a doublet centered at τ 6.53 (H-C≡), a multiplet at τ 7.8-8.0 ($-CH_2-$) and a multiplet at τ 8.8-9.2 (CH_3-). The ratio of alkyl to ethynyl hydrogens was 18/1.

<u>Preparation of Trans-1,2-vinylenebis(di-n-butylphosphine) Monoxide. Method A. Via Reaction Between Di-n-butylethynylphosphine Oxide and Di-n-butylphosphine</u>. -- Solid di-n-butylethynylphosphine oxide (4.65 g, 0.025 mole) and 3.65 g (0.025 mole) of liquid di-n-butylphosphine were placed in a 240 mm x 25 mm reaction tube which was equipped with a magnetic stirring bar. All precautions were taken to exclude oxygen during the addition of the reagents as well as during the course of the reaction. The heterogeneous mixture was stirred as the tube was warmed in an oil

bath at 80°. Within five minutes the contents of the flask appeared as a uniform clear solution, whereupon a vigorous reaction appeared to take place. The oil bath was quickly removed. Stirring was continued for another fifteen minutes, as the solution cooled to room temperature. At this point, the reaction was considered to have been completed.

In order to remove any unreacted starting materials, the contents of the reaction tube were heated in vacuo at 80°. The viscous oil was stirred vigorously in order to minimize splattering. After one night under these conditions, the temperature was increased to 160°, and a white solid collected on the walls of the tube. However, some splattering of the dark oil was unavoidable, and this finally led to some contamination of the collected solid. After twenty-four hours, 4.1 g of crude reaction product had been collected. This was placed in a sublimator and reheated at 90-100°/0.02 mm. At this temperature, a small amount of colorless liquid distilled from the solid and was observed along the walls of the sublimation apparatus. The solid was heated at this temperature and pressure until the liquid was no longer observed. The residue was then sublimed at 140°/0.02 mm and 3.0 g of a crystalline solid, m.p. 100-105° was obtained. The solid was then crystallized from hexane and resublimed at 140°/0.02 mm yielding 1.8 g (21%) of trans-1,2-vinylenebis-(di-n-butylphosphine) monoxide, m.p. 107-109°. The nmr spectrum ($CDCl_3$) exhibited sixteen peaks at τ 2.15-4.30 (), a multiplet at τ 8.05-8.75 ($-CH_2-$) and a multiplet at τ 8.88-9.31 (CH_3-). The ratio of alkyl to vinyl hydrogens was 18/1.

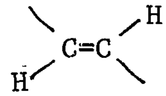
Anal. Calcd for $C_{18}H_{38}P_2O$: C, 65.03; H, 11.52; P, 18.63. Found: C, 65.32; H, 11.51; P, 18.40.

Preparation of Di-n-butylphosphine Oxide. -- The method used by Williams[81] to prepare long chain dialkylphosphine oxides, $(C_nH_{2n+2})_2PH$ where $n \geqslant 6$, was adapted for the following procedure. Diethylphosphite* (83.5 g, 0.60 mole), b.p. 58°/6 mm, (reported b.p. 82°/18)[82] in 300 ml of ether was slowly added to a solution containing two moles of n-butylmagnesium bromide prepared from 48.0 g (2.0 moles) of magnesium and 268.g (2.0 moles) of n-butyl bromide in 1800 ml of ether. The rate of addition was adjusted to allow gentle refluxing of the solvent. After the addition had been completed, the contents of the flask were stirred for two more hours. The ether was then treated with a saturated ammonium chloride solution and dried over anhydrous sodium sulfate. Upon removal of the ether, a yellow oil was obtained which after four crystallizations from hexane yielded 6.0 g (6%) of white, crystalline di-n-butylphosphine oxide, m.p. 62-63°. Reported,[83] m.p. 55-58°. The nmr spectrum ($CDCl_3$) exhibited a doublet centered at τ 6.40 (H-P), a multiplet at τ 7.80-8.81 ($-CH_2-$), and a multiplet at τ 8.85-9.20 (CH_3-). The ratio of alkyl to phosphine oxide hydrogens was 18/1.

Preparation of Trans-1,2-vinylenebis(di-n-butylphosphine) Monoxide. Method B. Via Reaction Between Di-n-butylethynylphosphine and Di-n-butylphosphine Oxide. -- A 240 mm x 25 mm reaction tube equipped with a magnetic stirrer was charged with 1.63 g (0.010 mole) if di-n-butylphosphine oxide, 1.70 g (0.010 mole) of di-n-butylethynylphosphine and 0.16 g (0.01 mole) of azo-bis-isobutyronitrile. The flask was placed in an oil bath at room temperature, and the reactants were stirred. The oil bath

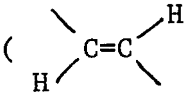
---

*Purchased from K & K Laboratories, Plainview, New York.

was heated slowly, and at 80° the solution in the flask started to darken in color. Stirring and heating were continued until the oil bath reached 110°. At this point, the oil bath was removed and the contents of the flask were allowed to cool to room temperature. The crude reaction product appeared as a dark viscous oil. This was then sublimed directly in the reaction tube at 140°/0.02 mm. The semi-solid material that collected along the walls of the flask was then placed in a sublimation apparatus and heated to 100° <u>in vacuo</u> to remove unreacted starting material. The remaining solid was then sublimed at 130°/0.02 mm, and resublimed at 130°/0.02 mm to yield 0.50 g (17%) of trans-1,2-vinylenebis(di-n-butylphosphine) monoxide, m.p. 107-108°. A mixed melting point determination with the monoxide prepared via method A showed no depression. The nmr spectra ($CDCl_3$) exhibited sixteen peaks at τ 2.15-4.30 (), a multiplet at τ 8.05-8.75 ($-CH_2-$), and a multiplet at τ 8.88-9.31 (CH_3-). The ratio of alkyl to vinyl hydrogens was 18/1.

<u>Anal</u>. Calcd for $C_{18}H_{38}P_2O$: C, 65.03; H, 11.52; P, 18.63. Found: C, 64.92; H, 11.73; P, 18.46.

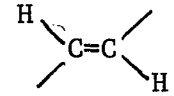
<u>Preparation of Trans-1,2-vinylenebis(di-n-butylphosphine) Dioxide</u>. <u>Method A. Via Trans-1,2-vinylenebis(di-n-butylphosphine) Monoxide and Hydrogen Peroxide</u>. -- To a mixture of 0.50 g (0.0016 mole) of trans-1,2-vinylenebis(di-n-butylphosphine) monoxide and 50 ml of acetone was added a solution of 3.0 g (0.03 mole) of 30% hydrogen peroxide in 10 ml of acetone. As the hydrogen peroxide solution was added, all the monoxide dissolved. After the addition had been completed, the mixture was warmed slightly and stirred for thirty minutes. All volatiles were removed <u>in vacuo</u> leaving 0.5 g of a white, crystalline, solid m.p. 259-260°. One

sublimation of this compound at 230°/0.02 mm yielded 0.45 g (89%) of trans-1,2-vinylenebis(di-n-butylphosphine) dioxide, m.p. 266-267°. The nmr spectrum ($CDCl_3$) exhibited a triplet centered at τ 2.95 (), a multiplet at τ 8.0-8.8 ($-CH_2-$), and a multiplet at τ 8.8-9.2 (CH_3-). The ratio of alkyl to vinyl hydrogens was 18/1.

Anal. Calcd for $C_{18}H_{38}P_2O_2$: C, 62.04; H, 10.99; P, 17.77. Found: C, 61.76; H, 11.24; P, 17.99.

Preparation of Trans-1,2-vinylenebis(di-n-butylphosphine) Dioxide. Method B. Via Trans-1,2-vinylenebis(di-n-butylphosphine) and Hydrogen Peroxide. -- To a solution of 0.20 g (0.00063 mole) of trans-1,2-vinylenebis(di-n-butylphosphine) in 15 ml of acetone was added a solution of 1.0 g (0.01 mole) of 30% hydrogen peroxide in 10 ml of acetone. After the first drops of hydrogen peroxide solution were added, heat was evolved and a white solid separated from the solution. When the addition had been completed, the white solid material redissolved. The solvent was removed *in vacuo*, leaving 0.20 g of a white, crystalline solid, m.p. 255-257°. Sublimation of this solid at 230°/0.02 mm yielded 0.19 g (90%) of trans-1,2-vinylenebis(di-n-butylphosphine) dioxide, m.p. 266-267°. A mixed melting point determination with a sample from the oxidation of the monoxide showed no depression of the melting point. The nmr spectra of the two samples were also identical.

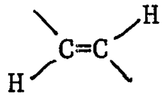
Anal. Calcd for $C_{18}H_{38}P_2O_2$: C, 62.04; H, 10.99; P, 17.77. Found: C, 61.82; H, 10.84; P, 17.58.

Preparation of Trans-1,2-vinylenebis(di-n-butylmethylphosphonium) Diiodide. -- Methyl iodide (2.5 g, 0.017 mole) was added to a solution containing 1.2 g (0.0038 mole) of trans-1,2-vinylenebis(di-n-butylphosphine) in 20 ml of methyl alcohol. The addition was accompanied by the evolution of heat. Stirring was continued for thirty minutes after the addition had been completed. The solvent was then removed in vacuo. Two crystallizations from a methyl alcohol-water mixture yielded 1.8 g (82%) of trans-1,2-vinylenebis(di-n-butylmethylphosphonium) diiodide, m.p. 130-132°. The nmr spectrum (CD_3OD) exhibited a triplet centered at τ 2.0 (), a multiplet at τ 7.3-9.0 ($-CH_2-$), a doublet centered at τ 8.0 (CH_3-P), and a multiplet at τ 8.8-9.2 (CH_3-).

Anal. Calcd for $C_{20}H_{44}P_2I_2$: C, 40.01; H, 7.38; I, 42.28. Found: C, 39.62; H, 7.72; I, 42.43.

Preparation of Di-n-butylmethyl(trans-β-di-n-butylphosphinoxy)-vinylphosphonium Iodide. -- To a solution containing 0.65 g (0.0019 mole) of trans-1,2-vinylenebis(di-n-butylphosphine) monoxide in 20 ml of methyl alcohol, was added an excess of methyl iodide (~ 3 g). The solution was stirred for forty-eight hours under a nitrogen atmosphere. All volatiles were removed in vacuo leaving a solid residue. This material was then washed in hot hexane and yielded 0.80 g of a yellow solid, m.p. 80-82°. Upon one crystallization from a methyl alcohol-acetone mixture 0.75 g (83%) of di-n-butylmethyl(trans-β-di-n-butylphosphinoxy)vinylphosphonium iodide was obtained, m.p. 82-83°.

Anal. Calcd for $C_{19}H_{41}P_2OI$: C, 48.10; H, 8.71; I, 26.75. Found: C, 47.94; H, 8.75; I, 26.71.

Preparation of Di-n-butylmethyl(trans-β-di-n-butylphosphinoxy)-vinylphosphonium Bromide. -- To a solution containing 2.15 g (0.0065 mole) of trans-1,2-vinylenebis(di-n-butylphosphine) monoxide in 20 ml of acetone, was added an excess of methyl bromide (~ 6 g). The solution was stirred overnight under a nitrogen atmosphere. After removal of the solvent in vacuo, 2.0 g of a white solid remained, m.p. 82-96°. Upon three crystallizations from acetone, 1.25 g (52%) of di-n-butylmethyl(trans-β-di-n-butylphosphinoxy)vinylphosphonium bromide was obtained, m.p. 102-104°. The nmr spectrum (CD_3OD) exhibited a multiplet at τ 2.15-3.91 (), a multiplet at τ 7.56-9.23 ($-CH_2-$), a doublet centered at τ 8.22 ($P-CH_3$), and a multiplet at τ 9.28-9.60 ($-CH_2-CH_3$).

Anal. Calcd for $C_{19}H_{41}P_2OBr$: C, 53.39; H, 9.66; Br, 18.69. Found: C, 53.26; H, 9.89; Br, 18.80.

Reaction of Di-n-butylmethyl(trans-β-di-n-butylphosphinoxy)-vinylphosphonium Bromide with Trichlorosilane. -- A mixture containing 0.60 g (0.0015 mole) of di-n-butylmethyl(trans-β-di-n-butylphosphinoxy)-vinylphosphonium bromide and 0.70 g (0.0045 mole) of trichlorosilane* in 30 ml of anhydrous benzene was stirred at room temperature under an atmosphere of nitrogen. After thirty minutes, approximately 10 ml of distilled water was added. This caused the formation of a white solid. All liquids were then evaporated from the flask in vacuo. The dry solid was washed with three 20 ml portions of hot acetone,** the washings were combined, and the acetone removed in vacuo. A solid residue remained which

---

*Purchased from K & K Laboratories, Plainview, New York.

**The insoluble material melted above 250°.

melted between 80-120°. An nmr spectrum of this material showed no vinyl hydrogens. A comparison of its infrared spectrum with that of starting material indicated that there was no phosphorus-oxygen bond in the molecule. Moreover, the observed infrared absorption peaks at 2200 cm^{-1} (γ_{Si-O}) and at 1100-1200 cm^{-1} (γ_{Si-H})[84] clearly demonstrated the presence of silicon in the molecule. From the above spectral information, it was concluded that either trichlorosilane added across the vinyl group or that cleavage was occurring.

Essentially the same results were obtained when phenylsilane in refluxing benzene was used instead of trichlorosilane. No reaction was observed with phenylsilane at room temperature.

Preparation of Diethylarsine. -- The same procedure was used as described in the reduction of tetra-n-butylbi(phosphine sulfide) with lithium aluminum hydride. A solution of 47.4 g (0.22 mole) of diethylbromoarsine (preparation described elsewhere) in 100 ml of ether was added slowly to a mixture of 10.0 g (0.26 mole) of lithium aluminum hydride in 150 ml of ether. From this reaction 11.3 g (39%) of diethylarsine, b.p. 106-108° was obtained (reported,[85] b.p. 101-107°).

Preparation of Tetraethylbiarsine. -- A solution of 0.084 mole of phenyllithium in 93 ml of ether was slowly added to 11.3 g (0.084 mole) of diethylarsine in 50 ml of ether.* After the addition had been completed, the ether was replaced with tetrahydrofuran, using the same procedure described in the preparation of lithium di-n-butylphosphide.

---

*Lithium di-n-butylphosphide has been previously prepared by this method.[86]

The lithium diethylarsenide reagent in 100 ml of tetrahydrofuran was added to 4.0 g (0.042 mole) of trans-1,2-dichloroethylene in 100 ml of tetrahydrofuran. The addition was carried out at -78°. The reaction product was then isolated in the usual manner. Two distillations of the crude liquid obtained from the reaction yielded 4.2 g (38%) of tetraethylbiarsine, b.p. 54°/0.2 mm. Reported,[87] b.p. 185-190°. The nmr spectrum (neat) exhibited only alkyl hydrogens.

Anal. Calcd for $C_8H_{20}As_2$: C, 36.10; H, 7.57. Found: C, 35.82; H, 7.32.

APPENDIX

LIST OF NEW COMPOUNDS[a]

Compound	Bp(mm) or mp °C	Calcd %		Found %	
		C	H	C	H
$C_3F_7As(C_2H_3)_2$ [b]	44 (40)	28.21	2.02	28.44	2.17
$CH_3As(C_2H_3)_2$	102(760)	41.56	6.29	41.94	6.36
$C_2H_5As(C_2H_3)_2$	54(40)	45.59	7.01	45.74	7.07
$C_6H_5As(C_2H_3)_2$	44(0.3)	58.27	5.37	58.41	5.50
$(CH_3)_2AsC_2H_3$	79-80(760)	36.38	6.87	36.57	6.84
$(C_2H_5)_2AsC_2H_3$	58(39)	45.01	8.19	45.27	8.24
$n\text{-}C_4H_9P(C_2H_3)_2$	49-50(11)	67.58	10.63	67.58	10.42
$(C_2H_3)_3PO$	99-101	56.25	7.08	55.77	7.05
$n\text{-}C_4H_9As(O)(C_2H_3)_2$	66-67	47.54	7.48	47.40	7.27
$(C_2H_5)_2As(O)C_2H_3$	95-96	40.93	7.44	41.04	7.50
$(n\text{-}C_4H_9)_2PCH{=}CHP(n\text{-}C_4H_9)_2$	123-125(0.05)	68.31	12.10	68.49	12.20
$(n\text{-}C_4H_9)_2PCH{=}CHP(O)(n\text{-}C_4H_9)_2$ [c]	107-109	65.03	11.52	65.32	11.51
$(n\text{-}C_4H_9)_2P(O)CH{=}CHP(O)(n\text{-}C_4H_9)_2$ [d]	266-267	62.04	10.99	61.76	11.24
$(n\text{-}C_4H_9)_2(CH_3)\overset{+}{P}CH{=}CH\overset{+}{P}(CH_3)(n\text{-}C_4H_9)_2\ 2I^-$ [e]	130-132	40.01	7.38	39.62	7.72
$(n\text{-}C_4H_9)_2(CH_3)\overset{+}{P}CH{=}CHP(O)(n\text{-}C_4H_9)_2\ Br^-$ [f]	102-104	53.39	9.66	53.26	9.89
$(n\text{-}C_4H_9)_2(CH_3)\overset{+}{P}CH{=}CHP(O)(n\text{-}C_4H_9)_2\ I^-$ [g]	82-83	48.10	8.71		

[a] All vinylene compounds have trans configuration.

[b] *Anal.* Calcd for $C_7H_6F_7As$: F, 44.61. Found: F, 44.45.

[c] *Anal.* Calcd for $C_{18}H_{38}P_2O$: P, 18.63. Found: P, 18.40.

[d] *Anal.* Calcd for $C_{18}H_{38}P_2O_2$: P, 17.77. Found: P, 17.99.

[e] *Anal.* Calcd for $C_{20}H_{44}P_2I_2$: I, 42.28. Found: I, 42.43.

[f] *Anal.* Calcd for $C_{19}H_{41}P_2OBr$: Br, 18.69. Found: Br, 18.80.

[g] *Anal.* Calcd for $C_{19}H_{41}P_2OI$: I, 26.75. Found: I, 26.71.

BIBLIOGRAPHY

1. C. M. Humphries, A. D. Walsh, and P. A. Warsop, *Discussions Faraday Soc.*, **35**, 148 (1963); See also D. P. Stevenson, G. M. Coppinger, and J. W. Forbes, *J. Am. Chem. Soc.*, **83**, 4350 (1961).
2. M. Halman, *J. Chem. Soc.*, 2853 (1963).
3. C. N. R. Rao, "Ultraviolet and Visible Spectroscopy," Butterworth Publishers LTD., London, England, 1961, p. 15.
4. C. Charrier, M-P. Simonnin, W. Chodkiewicz, and P. Cadiot, *Compt. Rend.*, **258**, 1537 (1964).
5. See also C. Charrier, W. Chodkiewicz, and P. Cadiot, *Bull. Soc. Chim. France*, 1002 (1966).
6. K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).
7. H. H. Jaffe, *J. Chem. Phys.*, **22**, 1430 (1954); H. H. Jaffe, L. D. Freedman, *J. Am. Chem. Soc.*, **74**, 1069, 2930 (1952).
8. C. N. R. Rao, J. Ramachandran, and A. Balasubramanlan, *Can. J. Chem.*, **39**, 171 (1961); C. N. R. Rao, J. Ramachandran, M. S. C. Jah, S. Samosekkara, and N. Rajakumar, *Nature*, London **183**, 1475 (1959).
9. H. Schindlbaur, *Monatsh. Chem.*, **94**, 99 (1963).
10. H. Schindlbaur, *Monatsh. Chem.*, **96**, 1796 (1965); See also H. Schindlbaur and H. Hagen, *Monatsh. Chem.*, **96**, 285 (1965).
11. E. J. Halpern and K. Mislow, *J. Am. Chem. Soc.*, **89**, 5224 (1967).
12. H. Goetz, F. Nerdel, and K.-H. Wiechel, *Ann.*, **665**, 1 (1963).
13. Reference 12, p. 9.
14. G. P. Schiemenz, *Tetrahedron Letters*, 2729 (1964).
15. J. J. Monagle, J. V. Mengenhauser, and D. A. Jones Jr., *J. Org. Chem.*, **32**, 2477 (1967).
16. H. S. Shieh, Ph.D. Thesis, University of Pittsburgh, 1964.
17. C. E. Griffin, R. P. Peller, K. R. Martin, J. A. Peters, *J. Org. Chem.*, **30**, 97 (1965).
18. W. R. Cullen and R. M. Hochstrasser, *J. Mol. Spectr.*, **5**, 118 (1960); See also W. R. Cullen, B. R. Green, R. M. Hochstrasser, *J. Inorg. Nucl. Chem.*, **27**, 641 (1965).
19. F. Halverson and R. C. Hirt, *J. Chem. Phys.*, **19**, 711 (1951).

20. G. Shaw, *Chem. Commun.*, 425 (1966).

21. D. W. Turner in "Determination of Organic Structures by Physical Methods" Vol. 2, F. C. Nachod and W. D. Philips Ed., Academic Press, Inc., New York, N.Y., 1962, p. 364.

22. N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1006 (1954).

23. E. M. Popov, E. N. Tsvetkov, Chung-Yu-Chang, and T. Ya. Medred, *J. Gen. Chem. U.S.S.R.* (*English Transl.*), **32**, 3199 (1962).

24. Although earlier workers had reported a weak band between 220 and 230mμ in the spectrum of PH_3 G. H. Cheesman and H. J. Emeleus, *J. Chem. Soc.*, 2847 (1932); H. Melville, *Nature*, **129**, 546 (1932), this observation has not been verified in subsequent studies; see ref. 1.

25. F. A. Matsen in "Technique of Organic Chemistry" Vol. 9, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N.Y. 1956, p. 649.

26. G. Opitz, H. Hellman, and H. W. Schubert, *Ann.*, **623**, 112 (1959).

27. C. D. Good and D. M. Ritter, *J. Am. Chem. Soc.*, **84**, 1162 (1962).

28. Charles C. Price and Shigeru Oae, "Sulfur Bonding," The Ronald Press Company, New York, N.Y., 1962, See appendix.

29. C. E. Scott and C. C. Price, *J. Am. Chem. Soc.*, **81**, 2672 (1959). See pages 30-60.

30. Reference 29, p. 49.

31. R. F. Hudson "Structure and Mechanism in Organo-Phosphorus Chemistry" Vol. 6, Academic Press, Inc., New York, N.Y., 1965. p. 12.

32. W. R. Cullen in "Advances in Organometallic Chemistry," Vol. 4, F. G. A. Stone and R. West, Ed., Academic Press, Inc., New York, N.Y. 1966, p. 145.

33. a) J. Singh and A. B. Burg, *J. Am. Chem. Soc.*, **88**, 718 (1966).
    b) T. D. Goldfarb and S. Sujishi, *J. Am. Chem. Soc.*, **86**, 1679 (1964).
    c) J. E. Griffiths and K. B. McAfee, *Proc. Chem. Soc.*, 456 (1961).
    d) J. E. Griffiths and M. Onyszchuk, *Can. J. Chem.*, **39**, 339 (1961).
    e) A. N. Johnson, *J. Org. Chem.*, **25**, 183 (1960).

34. D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).

35. D. P. Craig, *J. Chem. Soc.*, 4895 (1956).

36. L. Maier, D. Seyferth, F. G. A. Stone, and E. G. Rochow, *J. Am. Chem. Soc.*, **69**, 5884 (1957).

37. G. P. van der Kelen, *Bull. Soc. Chim. Belges*, **65**, 343 (1956).

38. H. Hartman and G. Nowak, *Z. anorg. u allgem. chem.*, **290**, 348 (1957).

39. C. K. Banks, J. F. Morgan, R. L. Clark, E. B. Hatlelid, F. H. Kahler, H. W. Paxton, E. J. Crague, R. J. Andres, Bill Elpern, R. F. Coles, James Lawhead, and Cliff S. Hamilton, *J. Am. Chem. Soc.*, **69**, 927 (1947).

40. W. R. Cullen, *Can. J. Chem.*, **38**, 439 (1960).

41. L. Maier, *J. Inorg. Nucl. Chem.*, **24**, 1073 (1962).

42. P. J. Christen, L. M. Van Der Linde and F. N. Hooge, *Rec. Trav. Chim.*, **78**, 161 (1959).

43. K. A. Pollart and H. J. Harwood, *J. Org. Chem.*, **27**, 4446 (1962).

44. H. E. Ulmer, L. C. D. Groenweshe and L. Maier, *J. Inorg. Nucl. Chem.*, **20**, 82 (1961).

45. R. B. Fox, *J. Am. Chem. Soc.*, **72**, 4147 (1950).

46. D. J. Foster, *Brit. Patent*, 870, 425 (1961).

47. H. D. Kaesz and F. G. A. Stone, *J. Org. Chem.*, **24**, 635 (1959).

48. H. E. Ramsdem, *Brit. Patent*, 869, 528 (1961).

49. "Topics in Phosphorus Chemistry," Vol. 1, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N.Y., 1964, p. 19.

50. C. Screttas and A. F. Isbell, *J. Org. Chem.*, **27**, 2573 (1962).

51. A. Merijanian and R. A. Zingaro, *Inorg. Chem.*, **5**, 187 (1966).

52. J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

53. S. Rosenberg, A. Gibbons, and H. Ramsdem, *J. Am. Chem. Soc.* **79**, 2137 (1957).

54. K. Ziegler and H. Colonius, *Ann.*, **479**, 135 (1930).

55. D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **83**, 3583 (1961).

56. H. Normant, *Compt. Rend.*, **239**, 1510 (1954).

57. J. C. Bailar in "Inorganic Synthesis" Vol. 1, McGraw Hill Book Company, New York, N.Y., 1946, p. 103.

58. I. L. Knunyants, V. Ya. Pil'skaya, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 417 (1955).

59. F. Knotz, Osterr. Chemiker - Z., 50, 128 (1949).

60. J. A. Mastrjukova, A. E. Shipov and M. I. Kabachnik, Z. Obsc. Chim., 31, 507 (1961).

61. K. Issleib and W. Seidel, Ber., 92, 2681 (1959).

62. A. W. Frank, J. Org. Chem., 26, 850 (1961).

63. W. A. Henderson Jr., S. A. Buckler, N. E. Day, and M. Grayson, J. Org. Chem., 26, 4770 (1961).

64. M. I. Kabachnik, Chung-Yu-Chang and E. N. Tsvetkov, Doklady Akad. Nauk. S.S.S.R., 135, 603 (1960); C. A., 55, 12,272a (1961).

65. T. Weil, B. Prijs, H. Erlenmeyer, Helv. Chem. Acta, 36, 1314 (1953).

66. D. J. Peterson and H. R. Hays, J. Org. Chem., 30, 1939 (1965).

67. D. J. Peterson, J. Org. Chem., 31, 950 (1966).

68. M. I. Kabachnik, Tetrahedron, 20, 655 (1965).

69. A. M. Aguiar and D. Daigle, J. Am. Chem. Soc., 86, 2299 (1964).

70. K. Isslieb and D. W. Muller, Ber., 92, 3175 (1959).

71. W. Hewertson and H. R. Watson, J. Chem. Soc., 1490 (1962).

72. A. J. Leusink, H. A. Budding, and W. Drenth, J. Organometal. Chem., 11, 541 (1968); Additional references there-in.

73. "The Organic Chemistry of Phosphorus," A. J. Kirby and S. G. Warren, Elsevier Publishing Company, New York, N.Y., p. 158.

74. H. Fritzsche, U. Hasserodt and F. Korte, Ber. 97, 1988 (1964).

75. a) K. Issleib and F. Krech, Ber., 94, 2656 (1961).
b) A. M. Aguiar, K. C. Hansen and J. T. Mague, J. Org. Chem., 32, 2383 (1967).

76. K. Issleib and A. Tzschach, Ber., 92, 704 (1959).

77. K. Issleib and A. Tzschach, Ber., 92, 1118 (1959).

78. K. Issleib and W. Seidel, Ber., 92, 2681 (1959).

79. W. Voskuil and J. F. Arens, Rec. Trav. Chim., 88, 993 (1962).

80. Private Communication - W. Hagens, Rijhsuniversiteit Utrecht, Utrecht, Netherlands.

81. R. H. Williams and L. A. Hamilton, J. Am. Chem. Soc., 74, 5418 (1952).

82. V. F. Cooke, W. Gerrard, J. Chem. Soc., 1978 (1955).

83. M. Sander, Ber., 93, 1220 (1960).

84. "Handbook of Organic Structural Analysis" Ed. Yasuhide Yukawa, W. A. Benjamin, Publishing Company, New York, N.Y., pp. 446-447.

85. A. Tzschach and W. Lange, Z. Anorg. Allgem. Chem., 326, 280 (1964).

86. A. Tzschach and W. Peylig, Z. Anorg. Allgem. Chem., 336, 36 (1965); See also A. Tzschach and W. Lange, Z. Anorg. Allgem. Chem., 330, 317 (1964).

87. Cahours and Riche, Ann., 92, 365 (1854).

AUTOBIOGRAPHICAL STATEMENT

The author was born January 12, 1937 in New York City. He attended elementary school in Bronx, New York, and later graduated from Herman Ritter Junior High School and Samuel Gompers High School, both also in Bronx.

He received his B.S. degree from the City College of New York, New York City, in June 1959. In February 1963, he was admitted into the Ph.D. program in chemistry at The City University of New York, where he was a teaching assistant (1963-1968). In 1968, he accepted a postdoctoral position with Professor C. E. Griffin at the University of Pittsburgh.