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ORGANOPHOSPHORUS COMPOUNDS CONTAINING ACETYLENIC AND DIENE SUBSTITUENTS

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CONTENTS

I. Introduction 249

II. Preparation and chemical properties 249
1. Phosphines 249
2. Phosphine oxides, sulphides, selenides, and quaternary salts 254
3. Phosphonous and phosphonic acids and their derivatives 254

III. Electronic interactions in organophosphorus compounds containing acetylenic and diene substituents 256

I. INTRODUCTION

The interest taken by research workers in the chemistry of unsaturated organophosphorus compounds, which has increased extraordinarily during recent years, is explained by the potentialities of these compounds for use as monomers in the manufacture of plastics[1], intermediates in the synthesis of plasticisers[2], solvents for the extraction of compounds of the rare metals[3], finishing agents for textiles[4], additives to lubricating oils[5], and also as starting materials for the synthesis of various biologically active compounds[6-10]. Besides this, the great reactivity and the accessibility of unsaturated organophosphorus compounds of various classes makes them valuable materials for the study of the interaction of atoms in organic compounds of elements in the Third Period, in particular for elucidating the role of the vacant *d*-orbitals in the transmission of electronic influences in the molecule[11-14].

The first attempts to prepare acetylenic derivatives of phosphorus were made in 1921.[15] More recent work on the synthesis of tertiary acetylenic phosphines and of phosphonic esters containing 1,3-diene substituents attached to the phosphorus atom has been summarised in Gefter's monograph[1] (up to 1958) and in several reviews[16,17]. This section of the chemistry of organophosphorus compounds has developed so rapidly since 1958 that the number of compounds synthesised has more than doubled. During the past seven years original new routes have been worked out for the synthesis of highly unsaturated compounds containing acetylenic, allenic, and 1,3-diene substituents attached to the phosphorus atom. Data obtained from the study of unsaturated organic compounds of phosphorus by modern physical methods (ultraviolet, infrared, and nuclear magnetic resonance spectroscopy, dipole moments) have enabled certain conclusions to be drawn concerning the way in which phosphorus-containing groups are conjugated with multiple bonds. The present review summarises all these fresh results.

II. PREPARATION AND CHEMICAL PROPERTIES

1. Phosphines

Primary phosphines are usually obtained by the reduction of halogenophosphines and by the reaction of phosphine and its metal derivatives with alkyl halides and carbonyl compounds[18]. None of these methods has been used to obtain acetylenic or diene phosphines. Attempts to use the reduction of phenylethynylphosphonic ester with lithium tetrahydroaluminate to obtain a primary phosphine containing the phosphino-group directly linked to a triple bond were unsuccessful. Besides cleavage of the phosphorus–carbon bond, the triple bond was hydrogenated to a double bond with formation of α-styrylphosphine[19,20]:

$$C_6H_5C{\equiv}CPO(OC_2H_5)_2 \rightarrow C_6H_5CH{=}CHPH_2.$$

Two of the primary acetylenic phosphines which have been described were obtained by the reaction of sodium phosphide with acetylenic α-epoxides in liquid ammonia[21]:

$$RC{\equiv}C{-}\underset{CH_2}{\overset{O}{C}}{-}CH_2 \xrightarrow[NH_3]{NaPH_2} RC{\equiv}CC(OH)(CH_3)CH_2PH_2$$

where R = CH_3 or C_4H_9.

No secondary phosphines have been described containing acetylenic or diene substituents. Tertiary phosphines,

however, represent the most thoroughly studied group of phosphines both with saturated and with unsaturated substituents.

The most widely applicable method of preparing tertiary phosphines is the reaction of organometallic compounds with three-coordinated phosphorus halides. Most of the tertiary acetylenic phosphines have been obtained by this method. A long series of papers in this field was initiated by de Mahler [15], who tried to obtain phosphorus carbide by the reaction of ethynylenedimagnesium di-iodide with phosphorus trichloride. Although the desired result was not achieved in this case [22-24], the synthesis became the most fruitful method of obtaining various tertiary acetylenic phosphines. Successful use was subsequently made of Iotsich complexes derived from acetylenic hydrocarbons, acetylenic alcohols [25,26] and sulphides [27], ethynylmagnesium [27,28] and butadiynylmagnesium bromides in tetrahydrofuran, and also ethynylenedimagnesium dibromide [24,27,29]. From the appropriate organomagnesium compounds and diaryl- or dialkyl-phosphinous chlorides compounds could be obtained containing alkenynyl [30,31], butadiynyl, and hexatriynyl [30] substituents attached to the phosphorus atom, as well as acetylenic diphosphines [24,27,29]:

$$R\,[C{\equiv}C]_nMgX + R_2PCl \rightarrow R\,[C{\equiv}C]_nPR_2.$$

The application of this reaction to phenylphosphonous dichloride and to phosphorus trichloride enabled tertiary phosphines to be obtained containing two [25] and three [32] acetylenic substituents. The yields in reactions of this type are usually high. A diminished yield is often due to instability of the final products.

Sodium acetylides in liquid ammonia can be used instead of organomagnesium compounds. The chlorophosphines are then replaced as starting materials by the corresponding alkoxy- or alkylthio-derivatives [27]:

$$HC{\equiv}CNa + ROPR'_2 \rightarrow HC{\equiv}CPR'_2 + RONa.$$

It must be supposed that sodium alkyl or aryl acetylides may be used equally successfully in this interesting reaction.

Another original route has also been proposed for the preparation of tertiary phosphines containing a terminal acetylenic group. Cleavage of 4-diphenylphosphino-2-methylbut-3-yn-2-ol in the presence of alkali leads to the formation of ethynyldiphenylphosphine in 68% yield:

$$(C_6H_5)_2PC{\equiv}CC(CH_3)_2OH \xrightarrow{KOH} (C_6H_5)_2PC{\equiv}CH + (CH_3)_2CO.$$

Unfortunately, no experimental details are given [25]. Finally, bisdibutylphosphinoacetylene is cleaved by phenyl-lithium with the formation of dibutylphosphine and ethynyldibutylphosphine [27]:

$$(C_4H_9)_2PC{\equiv}CP(C_4H_9)_2 + C_6H_5Li \rightarrow (C_4H_9)_2PC{\equiv}CLi + C_6H_5P(C_4H_9)_2$$
$$\downarrow H_2O$$
$$(C_4H_9)_2PC{\equiv}CH$$

The above phosphines containing a terminal acetylenic group readily undergo substitution of the acetylenic hydrogen. This method has been used to synthesise tertiary alkylacetylenic phosphines and acetylenic carbinols containing a dialkylphosphino-group attached to the triple bond [25,27].

Tertiary acetylenic phosphines can also be obtained from the lithium dialkyl phosphide and chloroacetylenes [33]:

$$R_2PLi + ClC{\equiv}CC_6H_5 \rightarrow R_2PC{\equiv}CC_6H_5 + LiCl.$$

This reaction is less convenient for obtaining acetylenic phosphines than, say, the organomagnesium synthesis. However, it is of theoretical interest, since it indicates the quite high reactivity of a halogen adjacent to a triple bond. A reaction of similar type has proved extremely fruitful in the synthesis of esters of phosphonic acids containing acetylenic substituents.

Petrov and Kormer proposed a method for preparing tertiary phosphines having an allenic group in the hydrocarbon substituent, which was based on the addition of lithium phosphides to alka-1-en-3-ynes [34]:

$$RC{\equiv}CCH{=}CH_2 \xrightarrow{LiPR'_2} RLiC{=}C{=}CHCH_2PR'_2 \xrightarrow{H_2O} RCH{=}C{=}CHCH_2PR'_2,$$

where R = CH_3, C_2H_5 and R' = C_2H_5, C_4H_9. Pent-1-en-3-yne yields as side-product an acetylenic phosphine: i.e. allene–acetylene rearrangement is observed [35].

Among phosphines containing conjugated diene substituents, only cyclic phospholes are known. These are obtained by the reaction of tetraphenylbuta-1,3-dienylene-dilithium with dihalogenophosphines, or alternatively by the interaction of the 1,4-di-iodobutadiene derivative with disodium phenyl phosphide [36-39]:

$$\left.\begin{array}{l} LiC(C_6H_5){=}C(C_6H_5)C(C_6H_5){=}C(C_6H_5)Li + C_6H_5PCl_2 \\ IC(C_6H_5){=}C(C_6H_5)C(C_6H_5){=}C(C_6H_5)I + C_6H_5PNa_2 \end{array}\right\} \rightarrow \begin{array}{l} C_6H_5{-}C{-}C{-}C_6H_5 \\ C_6H_5{-}C\;\;\;C{-}C_6H_5. \\ \quad\quad P{-}C_6H_5 \end{array}$$

Heterocycles containing two conjugated double bonds and containing several heteroatoms besides phosphorus have been synthesised by this method.

It can thus be seen that methods for the synthesis of tertiary phosphines containing acetylenic or diene substituents are more varied than those for obtaining phosphines containing ethylenic substituents [40-45].

Acetylenic and diene phosphines are liquids or crystalline solids having the characteristic properties of phosphines. Those containing alkyl groups possess an unpleasant odour. The constants of the acetylenic and diene phosphines which have been described are given in Table 1. The only omissions from this are the phosphines mentioned in Ref. 30 without indication of their constants or yields (1-diethylphosphinopropyne, 1-diethylphosphino-2-phenylacetylene, and 1-diphenylphosphino-propyne, -butadiyne, -penta-1,3-diyne, and -hepta-1,3,5-triyne).

Little work has been done on the chemical properties of acetylenic phosphines. The strength of the phosphorus–carbon bond is strongly dependent on the structure of the phosphine. Thus bisdiphenylphosphinoacetylene is not cleaved by dilute alkali, silver nitrate, or cuprammonium solution; cleavage takes place only on alkaline fusion or prolonged boiling with a saturated alcoholic solution of potassium hydroxide [24]. Dibutylphosphinoacetylene disproportionates in the presence of alkaline catalysts in liquid ammonia, with the formation of bisdibutylphosphinoacetylene, which, as already noted, may be cleaved by butyl-lithium [27]. Heating 4-diphenylphosphino-2-methylbut-3-yn-2-ol with alkali leads to the elimination of acetone, as already mentioned, but does not affect the P–C≡ bond [25]. The enhanced stability of the phosphorus–acetylenic bond in comparison with acetylenic derivatives of other elements is explained by the small difference in electronegativities between carbon and phosphorus according to Pauling (2.8 and 2.1 respectively) [24], which can hardly be accepted as correct.

TABLE 1. Organophosphorus compounds containing acetylenic and diene radicals*.

Compound	Yield, %	B.p., °C (pressure, mmHg)	M.p., °C	d_4^{20}	n_D^{20}	Ref.
primary phosphines						
$CH_3C{\equiv}CC(OH)CH_2PH_2$	73	50—51 (1)	—	0.9880	1.5063	21
$n\text{-}C_4H_9C{\equiv}CC(OH)(CH_3)CH_2PH_2$	73	60—64 (0.5)	—	0.9360	1.5063	21
tertiary phosphines having a terminal acetylenic group						
$(C_6H_5)_2PC{\equiv}CH$	49	66—67 (77)	—	—	1.4808	27
$(n\text{-}C_3H_7)_2PC{\equiv}CH$	60	55 (11)	—	—	1.4770	27
$(n\text{-}C_4H_9)_2PC{\equiv}CH$	70	37 (0.3)	—	—	1.4765	27,29
$(n\text{-}C_5H_{11})_2PC{\equiv}CH$	72.5	65 (0.35)	—	—	1.4759	27
$(C_6H_5)_2PC{\equiv}CH$	68	—	35	—	—	25,32,40—43
tertiary phosphines having a disubstituted acetylenic group						
$(n\text{-}C_4H_9)_2PC{\equiv}CCH_3$	81	66—67 (1)	—	—	1.4867	27
$(n\text{-}C_4H_9)_2PC{\equiv}CC_2H_5$	84	58 (0.25)	—	—	1.4848	27
$(n\text{-}C_4H_9)_2PC{\equiv}CCH{=}CH_2$		92 (3)	—	0.8602	1.5110	31
$(n\text{-}C_4H_9)_2PC{\equiv}CSC_2H_5$	81	78 (10^{-3})	—	—	1.5265	27
$(n\text{-}C_4H_9)_2PC{\equiv}C-C_6H_5$	70	—	44	—	—	33
$(C_6H_5)_2PC{\equiv}CC_6H_5$	79	—	43	—	—	25, 26, 33
	50		44			
$(C_5H_{11})_2PC{\equiv}CC_6H_5$	35	—	74	—	—	33
tertiary phosphine derivatives of acetylenic carbinols						
$(n\text{-}C_4H_9)_2PC{\equiv}CC(OH)(CH_3)_2$	58	91 (0.03)	—	—	1.4871	27
$(n\text{-}C_4H_9)_2PC{\equiv}CC(OH)(CH_3)_2$	70	105 (10^{-3})	25	—	1.5090	27
$(C_6H_5)_2PC{\equiv}CC(OH)(C_6H_5)_2$	95	—	143	—	—	25
$C_2H_5)_2PC{\equiv}CCH(OH)R$ (where R = fluoren-9-yl)	85	—	133	—	—	25
$(C_6H_5)_2PC{\equiv}CXOH$ **	90	—	202	—	—	25
tertiary phosphines containing two or three acetylenic groups						
$(RCH_2C{\equiv}C)_2P-C_6H_5$ (where R = anthr-9-yl)	90	—	193	—	—	52
$(HC{\equiv}C)_3P$	—	52 (30)	36—37	—	—	28
$(C_6H_4C{\equiv}C)_3P$	90	—	91	—	—	28
$(p\text{-}CH_3C_6H_4C{\equiv}C)_3P$	—	—	125	—	—	32
$(p\text{-}ClC_6H_4C{\equiv}C)_3P$	—	—	192 (decomp.)	—	—	32
$(RCH_2C{\equiv}C)_3P$ (where R = anthr-9-yl)	89	—	256	—	—	28
acetylenic disphosphines						
$(n\text{-}C_4H_9)_2PC{\equiv}CP(C_6H_5\text{-}n)_2$	96	—	33	—	—	27, 29
$(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$	—	—	86	—	—	24
tertiary phosphines containing 1,2- and 1,3-diene groups						
$(C_6H_5)_2PCH_2CH{=}C{=}CHCH_3$	36.5	60—61 (5)	—	0.8697	1.5050	51
$(C_6H_5)_2PCH_2CH{=}C{=}CHC_2H_5$	34	78—79 (5)	—	0.8569	1.5025	51
$(n\text{-}C_4H_9)_2PCH_2CH{=}C{=}CHC_2H_5$	28	125—126 (5)	—	0.8534	1.4952	51
phosphine oxides, sulphides, selenides, and quaternary salts						
$(CH_3)_2P(O)CH{=}C{=}CH_2$	—		58—60	—	—	52
$(C_6H_5)_2P(O)CH{=}C{=}CH_2$	60		96—99	—	—	51
$(C_6H_5)_2P(O)CH{=}C{=}C(CH_3)_2$	75		70—73	—	—	51
$(C_6H_5)_2P(O)CH{=}C{=}C(CH_3)C_2H_5$	80		69—71	—	—	51
$(C_6H_5)_2P(O)CH{=}C{=}CHC_2H_7$	95		43—46	—	—	51
$(C_6H_5)_2P(O)CH{=}C{=}C(CH_3)_2$	90	—	107—109	—	—	51
$(C_6H_5)_2P(O)C{=}C{=}C(CH_3)C_2H_5$ $HOC(CH_3)C_2H_5$	90	—	—	—	1.5711	51
$(p\text{-}Cl{-}C_6H_4)_2P(O){-}C{=}C{=}C(CH_3)C_2H_5$ $HOC(CH_3)C_2H_5$	99	—	—	—	—	51
$(C_6H_5)_2P(O)C{=}CP(O)(C_6H_5)_2$	87	—	164	—	—	23
$(p\text{-}CH_3C_6H_4C{=}C)_3P{=}O$	—	—	177	—	—	32
$(C_6H_5)_2P(S)C{=}CC_6H_5$	quantitative	—	156	—	—	33
$(C_5H_{11})_2P(S)C{=}CC_6H_5$	quantitative	—	111.5	—	—	33
$(C_6H_5)_2P(S)C{=}CP(S)(C_6H_5)_2$	75	—	186	—	—	23
$(p\text{-}CH_3C_6H_4C{=}C)_3P{=}S$	—	—	180 (decomp.)	—	—	32
$(p\text{-}CH_3C_6H_4C{=}C)_3P{=}Se$	—	—	162 (decomp.)	—	—	32
$[(C_6H_5)_2P(CH_3)C{=}CP(C_6H_5)_2]{+}I^-$	90	—	156	—	—	23
$[(C_6H_5)_2P(C_2H_5)C{=}CP(C_6H_5)_2]{+}I^-$	84	—	128	—	—	34
$(C_6H_4C{=}C)_2PS$	50		138.4—138.8	—	—	47
$[2,4\text{-}(CH_3)_2C_6H_3C{=}C]_2PS$	70	—	144.4—145.0	—	—	53
$(CH_3C{=}C)_2PS$	35	—	198.4—198.8	—	—	47
$C_6H_5P(S)(C{=}CC_6H_5)_2$	85	—	129.6—130.0	—	—	47
$C_6H_5P(S)(C{=}CCH{=}CH_2)_2$	30	—	67.8—68.4	—	—	47
$C_6H_5CH{=}CHP(S)(C{=}CC_6H_5)_2$	61	—	183.0—183.4	—	—	48
$CH_3P(S)(C{=}CCH_3)_2$	28	—	38.2—38.8	—	—	48
$CH_3P(S)(C{=}CC_6H_5)_2$	60	—	91.3—91.6	—	—	48
$(CH_3)_2P(S)C{=}CCH_3$	62	—	77.5—78.2	—	—	48
$(CH_3)_2P(S)C{=}CC_6H_5$	86	—	92.4—93.2	—	—	48
$(CH_3)_2P(S)C{=}CCH{=}CH_2$	63	122 (5)	42.0—43.0	1.0349	1.5852	48
$CH_3P(O)(C{=}CCH_3)_2$	55	—	70.5—71.0	—	—	49
$CH_3P(O)(C{=}CC_6H_5)_2$	65	—	101.0—101.4	—	—	49
esters of phosphonous acids containing acetylenic radicals						
$HC{=}CP(OC_4H_9\text{-}n)_2$	74	58.8—60 (2)	—	0.9829	1.4520	40—43
$HC{=}CP(OH)(OC_4H_9\text{-}n)$	78	65—66 (1.5)	—	1.0322	1.4492	40—43

TABLE 1 (contd.)

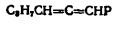
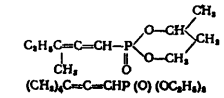
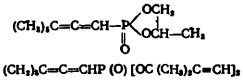
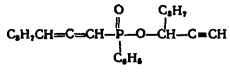
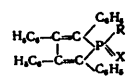
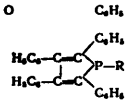
Compound	Yield, %	B.p., °C (pressure, mmHg)	M.p., °C	d_4^{20}	n_D^{20}	Ref.
phosphonic acids						
$C_6H_5C{\equiv}CP(O)(OH)_2$	—	—	142	—	—	54
$o\text{-}ClC_6H_4P(O)(OH)_2$	—	—	134	—	—	54
$C_6H_5C{\equiv}CP(O)(OH)C_6H_5$	quantitative	—	126—127	—	—	55
$(C_6H_5C{\equiv}C)_2P(O)OH$	79	—	145—146	—	—	55
esters of phosphonic acids containing acetylenic radicals						
$HC{\equiv}CP(O)(OC_2H_5)_2$	25	50—60 (0.1)	—	—	—	56,57
$HC{\equiv}CP(O)(OC_6H_7\text{-}iso)_2$	25—35	75—77 (0.1)	—	—	—	56,57
$ClC{\equiv}CP(O)(OC_2H_5)_2$	56	88.5—89.5 (2.5)	—	1.1439	1.4473	58
$CH_3C{\equiv}CP(O)(OC_2H_5)_2$	—	115—116 (4)	—	1.0734	1.4460	59—63
$CH_3C{\equiv}CP(O)(OC_3H_7\text{-}n)_2$	—	127—128 (4)	—	1.0279	1.4478	62
$CH_3C{\equiv}CP(O)(OC_4H_9\text{-}n)_2$	—	152—153 (6)	—	1.0029	1.4498	62
$CH_3C{\equiv}CCH_2P(O)(OC_2H_5)_2$	45—55	98 (3)	—	1.0489	1.4540	64
$C_2H_5{-}C{\equiv}CP(O)(OC_2H_5)_2$	35	115—117 (3)	—	1.0325	1.4470	58
$CH_2{=}CHC{\equiv}CP(O)(OC_2H_5)_2$	45—55	107—108 (2.5)	—	1.0630	1.4540	65
$CH_2CH{=}CHC{\equiv}CP(O)(OC_2H_5)_2$	45—55	112—115 (2)		1.0610	1.4790	64
$CH_3{-}C(CH_3){\equiv}CP(O)(OC_2H_5)_2$	45—55	110—111 (3)		1.0549	1.4696	64
$C_6H_5C{\equiv}CP(O)(OC_2H_5)_2$	—	155 (1)		1.1500	1.5312	66
$C_6H_5C{\equiv}CP(O)(OC_3H_7\text{-}iso)_2$	—	159—161 (1)		1.0423	1.5090	66
$CH_2CH{=}CHC{\equiv}CCH_2{-}PO(OC_2H_5)_2$	53	107—107.5 (2)		1.0588	1.4752	61
$CH_3C{\equiv}CP(O)(OC_2H_5)_2$	28	134.5—136.5 (1.5)		1.0735	1.4930	67
$C_6H_5C{\equiv}CC{\equiv}CP(O)(OC_2H_5)_2$	54	130—131 (0.5)		1.0215	1.4897	67
derivatives of phosphonic acids containing allenic radicals						
$CH_2{=}C{=}CHP(O)(OC_2H_5)_2$	—	89 (0.4)		—	1.4544	52
$CH_2{=}C{=}CHP(O)(OC_3H_7\text{-}iso)_2$	—	126—127 (9)		1.0330	1.4580	62,63
$CH_2{=}C{=}CHP(O)(OCH_2C{=}CH)_2$	—	117 (0.3)		—	1.4282 (25°)	52
$CH_2{=}C{=}CHP(O)[N(CH_3)_2]_2$	—	85 (0.17)		—	1.5046 (25°)	52
$CH_2C{=}C{=}CHP(O)(SCH_3)_2$	—	102 (0.3)		—	1.5840 (25°)	52
$CH_2{=}C{=}CHP(O)(C_2H_5)(OCH_2C{=}CH)$	—	108 (0.3)		—	1.5071 (25°)	52,62,63
$CH_3CH{=}C{=}CHP(O)(OC_2H_5)_2$	—	105 (1.0)		—	1.4797 (25°)	52
$CH_3{-}C{=}C(CH_3)P(O)(OC_2H_5)_2$	—	73 (0.1)		—	1.4587 (25°)	52,63
$CH_2{=}C{=}C(C_6H_5)P(O)(OC_2H_5)_2$	—					63
$(CH_3)_2C{=}C{=}CHP(O)(OC_2H_5)_2$	—	95 (0.8)		—	1.4588 (25°)	52
$(CH_3)_2C{=}C{=}CHP(O)(C_6H_5)(OCH_2C{\equiv}CH)$	60	—	—	—	1.5344	51
$(CH_3)_2C{=}C{=}CHP(O)[OC(CH_3)_2C{\equiv}CH]_2$	78	—	—	—	1.4859	51
$(CH_3)_2C{=}C{=}CHP(O)(OC_3H_7\text{-}iso)_2$	91	—	—	—	1.4917	51
$C_6H_7CH{=}C{=}CHP(O)$ 	95	—	—	—	1.4910	51
	94.5	—	—	—	1.4950	5
$(CH_3)_2C{=}C{=}CHP(O)(OC_2H_5)_2$	—	123 (0.2)	—	—	1.4738 (25°)	52
	85	—	89—91	—	—	51
$(CH_3)_2C{=}C{=}CHP(O)[OC(CH_3)_2C{\equiv}CH]_2$	88	—	78—91	—	—	51
	95	—	—	—	1.5325	51
phosphonic chlorides containing acetylenic and diene radicals						
$CH_3C{\equiv}CP(O)Cl_2$	92.5	56—57 (1.5)	—	1.3953	1.4912	68
$CH_2{=}CHC{\equiv}CP(O)Cl_2$	28	61—65 (2.5)	—	1.3784	1.5150	68
$C_2H_5{-}C{\equiv}CP(O)Cl_2$	36	121—124 (0.5)	—	1.3650	1.5938	68
$CH_2{=}CHCH{=}CHP(O)Cl_2$	60	65—66 (1)	—	1.3107	1.5413	68
$CH_2{=}CHC(CH_3){=}CHP(O)Cl_2$	67	77.5—78 (2)	—	1.2887	1.5400	68
$CH_3CH{=}CHCH{=}CHP(O)Cl_2$	56	97—100 (3—3.5)	46—48	—	—	68
$CH_2{=}CHCH{=}CHP(S)Cl_2$	37	86—88 (1.5—2)	—	1.2992	1.5842	68
$ROCH{=}C(POCl_2)CCl{=}CH_2$						
$R{=}CH_3$	31	48—48.5 (0.002)	—	1.4562	1.5826	69
C_2H_5	43	59.5—60.5 (0.012)	—	1.3682	1.5730	69
C_3H_7	46	69—69.5 (0.012)	—	1.3152	1.5635	69
C_4H_9	55	82—82.5 (0.020)	—	1.3078	1.5620	69
$RSCH{=}C(POCl_2)CCl{=}CH_2$						
$R{=}CH_3$	80	67—67.5 (0.02)	—	1.4950	—	70
C_2H_5	58	77—77.5 (0.02)	—	1.4156	—	70
C_3H_7	62	83—84 (0.02)	—	1.3634	—	70
C_4H_9	76	81—82 (0.002)	—	1.3222	—	70
$CH_3C(CH_2Cl)CCl{=}CHPOCl_2$	59	121 (3)	—	1.5400	1.5405	71
	54	132 (2)	—	1.4103	1.5808	72
esters of phosphonic acids containing 1,3-diene radicals						
$CH_3C(CH_2Cl)CCl{=}CHP(O)(OR)_2$						71
$R{=}CH_3$	69	136 (3)	—	1.3155	1.4957	
C_2H_5	73	142.5 (2)	—	1.2365	1.4838	
C_3H_7	67	158 (2)	—	1.1749	1.4805	
						72
$R{=}C_2H_5$	90.5	132 (1)	—	1.1688	1.5142	
C_3H_7	56	131 (1)	—	1.1235	1.5083	

TABLE 1 (contd.)

Compound	Yield, %	B.p., °C (pressure, mmHg)	M.p., °C	d_4^{20}	n_D^{20}	Ref.
esters of phosphonic acids containing 1,3-diene radicals						
$ROCH{=}CHCCl{=}CHPO(OR')_2$						73—76
$R{=}CH_3$ $R'{=}CH_3$	58	90—91 (0.01)	—	1.2702	1.5180	
C_2H_5 CH_3	70	75—76 (0.004)	—	1.2372	1.5150	
C_3H_7 CH_3	60	84—85 (0.006)	—	1.1972	1.5108	
C_4H_9 CH_3	70	79.5—81 (0.002)	—	1.1742	1.5057	
C_3H_7 C_2H_5	55	87—88 (0.006)	—	1.1252	1.4990	
C_4H_9 C_2H_5	64	90—91 (0.006)	—	1.1122	1.4970	
$RSCH{=}CHCCl{=}CHPO(OR')_2$						73—76
$R{=}CH_3$ $R'{=}CH_3$	44	78 (0.007)	—	1.3011	1.5791	
C_2H_5 CH_3	45	80—81 (0.0085)	—	1.2531	1.5700	
C_3H_7 CH_3	60	84—85 (0.005)	—	1.2248	1.5623	
C_4H_9 CH_3	53	83—84 (0.0002)	—	1.1960	1.5490	
CH_3 C_2H_5	57	80 (0.005)	—	1.2121	1.5498	
C_2H_5 C_2H_5	60	84 (0.004)	—	1.1861	1.5460	
C_3H_7 C_2H_5	52	84—86 (0.004)	—	1.1535	1.5436	
C_4H_9 C_2H_5	57	94—95 (0.004)	—	1.1411	1.5420	
CH_3 C_3H_7	58	84—84.5 (0.003)	—	1.1524	1.5412	
C_2H_5 C_3H_7	46	90 (0.005)	—	1.1574	1.5402	
C_3H_7 C_3H_7	35	87 (0.0003)	—	1.1114	1.5334	
C_4H_9 C_3H_7	60	93 (0.0002)	—	1.0983	1.5294	
CH_3 C_4H_9	46	78—79 (0.002)	—	1.1103	1.5302	
C_2H_5 C_4H_9	56	82 (0.0015)	—	1.1014	1.5294	
C_3H_7 C_4H_9	63	72 (0.0001)	—	1.0869	1.5270	
C_4H_9 C_4H_9	57	92 (0.008)	—	1.0770	1.5236	
C_2H_5 $CH_2{=}CHCH_2$	37	62 (0.007)	—	1.1756	1.5620	
C_3H_7 $CH_2{=}CHCH_2$	45	97.0—97.5 (0.005)	—	1.1570	1.5570	
C_4H_9 $CH_2{=}CHCH_2$	50	104—105 (0.003)	—	1.1353	1.5508	
C_2H_5 $HC{\equiv}CCH_2$	39	125—126 (0.009)	—	1.2531	1.5804	
C_3H_7 $HC{\equiv}CCH_2$	38.4	125—126 (0.0007)	—	1.2278	1.5895	
C_4H_9 $HC{\equiv}CCH_2$	40	130—130.5 (0.009)	—	1.2073	1.5827	
$CH_2CH{=}CHCH{=}CHP(O)(OCH_3)_2$	54	101—103 (2)	—	1.0661	1.4932	68
$CH_2{=}CHCH{=}CHP(R)(OR_1)$						77
$R{=}CH_3$	25—30	80 (2)	—	1.1109	1.5300	
$R{=}C_2H_5$	25—30	93.0—93.5 (2)	—	1.0234	1.4971	
$R{=}C_4H_9$	25—30	115 (3)	—	0.9968	1.4984	
$CH_2{=}CHCH{=}CHP(Se)(OCH_3)_2$	—	98—100 (3)	—	1.3343	1.5164	77
sulphides and amides of phosphonic and phosphonothioic acids						
$ROCH{=}CHCCl{=}CHPO[N(C_2H_5)_2]$						73—76
$R{=}C_2H_5$	50	104—105 (0.006)	—	1.0652	1.5110	
C_4H_9	50	108—109 (0.008)	—	1.0532	1.5100	
$RSCH{=}CHCCl{=}CHPOR'_2$						73—76
$R{=}C_2H_5$ $R'{=}SC_2H_5$	60	122—123 (0.015)	—	1.2702	—	
C_3H_7 SC_2H_5	55	128—129 (0.015)	—	1.2087	—	
C_4H_9 SC_2H_5	57	158—160 (0.018)	—	1.1545	—	
C_4H_9 SC_2H_5	62	148 (0.012)	—	1.1332	—	
C_2H_5 $-N(CH_2)_4-CH_2$	75	133 (0.015)	—	1.2706	1.6023	
C_3H_7 $-N(CH_2)_4-CH_2$	82	148 (0.015)	—	1.2550	1.5996	
C_4H_9 $-N(CH_2)_4-CH_2$	78	155 (0.015)	—	1.2389	1.5945	
CH_3 $N(C_2H_5)_2$	63	101 (0.009)	—	1.1107	1.5606	
C_2H_5 $N(C_2H_5)_2$	36	107 (0.007)	—	1.0992	1.5564	
C_3H_7 $N(C_2H_5)_2$	43	112 (0.005)	—	1.0916	1.5516	
C_4H_9 $N(C_2H_5)_2$	36	118 (0.006)	—	1.0690	1.5482	
derivatives of 1-phosphacyclopenta-2,4-diene						
						
X=O $R{=}CH_3$	10	240—245.5	—	—	—	39
S C_2H_5	88	197—198	—	—	—	39
Se C_2H_5	93	187—188.5	—	—	—	39
O $CH_2C_6H_5$	10	240.5—241.5	—	—	—	39
O C_6H_5—Fe(CO)$_3$	94	226—235 (decomp.)	—	—	—	39
O C_6H_5	70	292—293	—	—	—	38
						
$R{=}C_2H_5$	84	255—256	—	—	—	36
$C_2H_5Fe(CO)_4$	quantitative	186—188	—	—	—	39
$C_2H_5Fe(CO)_3$		210—215	—	—	—	39
$C_2H_5Fe_2(CO)_5$		178—183 (decomp.)	—	—	—	39
$CH_2C_6H_5$	38	203—213	—	—	—	39

* Table 1 does not include compounds cited in Geffer's monograph.[1]

** X = anthrafuchsone.

Primary acetylenic phosphines — derivatives of acetylenic alcohols — do not give derivatives with 2,4-dinitrobenzoyl chloride, toluene-*p*-sulphonyl chloride, phenyl isocyanate, or picric acid, nor are they hydrogenated over platinum black or Raney nickel[21]. Tertiary acetylenic phosphines, however, can react both at the phosphino--group and at the acetylenic group. They add oxygen, sulphur, selenium, and halogenated hydrocarbons at the phosphorus, and compounds having alkyl substituents attached to the phosphorus are more reactive than aromatic or alkatriynyl phosphines[24,30,32,33]. As stated previously, tertiary phosphines containing a terminal acetylenic group undergo reactions involving substitution of the acetylenic hydrogen. Thiols in the presence of peroxides add at the triple bond[27]:

$$(C_6H_5)_2PC{\equiv}CH + C_2H_5SH \rightarrow (C_6H_5)_2PCH{=}CHSC_2H_5.$$

The chemical properties of phospholes give no grounds for assuming that these compounds are appreciably aromatic in character. They undergo both reactions characteristic of conjugated dienes (Diels–Alder reaction, formation of complexes with iron carbonyls) and reactions involving the lone pair of electrons on the phosphorus (addition of oxygen, sulphur, and selenium and complex formation)[36-39].

It follows from the above survey of the chemical properties of acetylenic phosphines that study of the influence of the triple bond on the well-known chemical properties of phosphines has been far from adequate, while the literature contains no discussion at all of the problem of the steric structure of acetylenic phosphines. An X-ray examination of bisdiphenylphosphinoacetylene[46] has shown that this compound crystallises in monoclinic form with four formula units in the unit cell.

2. Phosphine Oxides, Sulphides, Selenides, and Quaternary Salts

These compounds are usually obtained by the addition of oxygen, sulphur, selenium, and halogenated hydrocarbons to phosphines.

Oxidation of bisdiethylphosphinoacetylene with hydrogen peroxide gives the dioxide of this compound, while reaction with elementary sulphur yields the disulphide. On interaction of this diphosphine with alkyl iodides, however, only mono-derivatives of the type $(C_6H_5)_2PC{:}CP(CH_3)(C_6H_5)_2I$ are formed[24].

The addition of oxygen, sulphur, and selenium to *para*--substituted trisphenylethynylphosphines[32] or to cyclic phospholes[36-39] also results in formation of the corresponding oxides, sulphides, and selenides.

Oxides and sulphides of phospholes have been obtained also directly from phosphonic and phosphonothioic chlorides respectively and the dilithium derivative of tetraphenylbutadiene. A similar path, without phosphines as intermediate products, has recently been used to obtain oxides and sulphides of tertiary acetylenic phosphines. When Iotsich complexes interact respectively with thiophosphoryl trichloride and the corresponding *P*-alkyl and *P*-aryl dichlorides and *PP*-dialkyl monochlorides, phosphine sulphides are obtained containing 1–3 acetylenic substituents and also conjugated alkenynyl radicals attached to the phosphorus atom[47-49]:

$$RC{\equiv}CMgX + R'_nP(S)X_{3-n} \rightarrow R'_nP(S)(C{\equiv}CR)_{3-n}.$$

It is interesting that tetrasubstituted diphosphine disulphides cannot be obtained when Iotsich complexes are used, in contrast to what occurs with alkylmagnesium halides. In this respect phenyl and styryl substituents occupy an intermediate position: when they are initial reactants, a phosphorus–phosphorus bond is formed only when one of them contains an alkyl substituent[49].

Reaction of phenylethynylmagnesium bromide with styrylphosphonothioic chloride yields a tertiary phosphine sulphide containing two triple bonds and one double bond in the α-position to the phosphorus atom[49].

1-Halogenoalkynes react with triphenylphosphine to form quaternary phosphonium salts containing an acetylenic substituent. Fluoroacetylene reacts considerably more rapidly than does chloroacetylene[50]:

$$(C_6H_5)_3P + HC{\equiv}CX \rightarrow [(C_6H_5)_3PC{\equiv}CH]^+X^-.$$

A novel case of the Arbuzov rearrangement of esters formed by acids containing three-coordinated phosphorus with alcohols of prop-2-ynyl type, accompanied by acetylene–allene isomerisation, was described in 1962. Use of dialkyl- and diaryl-chlorophosphines and various acetylenic carbinols yielded in this way phosphine oxides containing an allenic group attached to the phosphorus atom[51,52]. The mechanism of this reaction will be discussed below (in Subsection 3).

The physical constants of phosphine oxides, sulphides, and selenides and quaternary phosphonium salts containing acetylenic substituents adjacent to the phosphorus atom are given in Table 1.

The chemical properties of compounds of this type have been little studied. The strength of the P–C≡ bond is appreciably lower in phosphine oxides and sulphides than in the corresponding phosphines. Bisdiphenylphosphinoacetylene dioxide and disulphide are cleaved with the evolution of acetylene by boiling with alcoholic caustic potash and even when chromatographed on alkaline aluminium oxide[24]. The oxides, sulphides, and selenides of tri--*p*-tolylethynylphosphine and tri-*p*-chlorophenylethynylphosphine are cleaved at the P–C≡ bond by alkali, silver nitrate, and Ilosvay reagent[32].

3. Phosphonous and Phosphonic Acids and Their Derivatives

During recent years an intensive study has been made of phosphonous and especially phosphonic acids containing unsaturated substituents, as well as of their derivatives.

The starting materials for the synthesis of saturated phosphonous acids and their derivatives are usually phosphines or halogenophosphines, which are subjected to oxidation, hydrolysis, alcoholysis, etc. They are also obtained by the reaction of phosphorohalidites with organomagnesium or organolithium compounds.

A general method for preparing saturated phosphonic acids is the reaction of alkyl halides with trialkyl phosphites, sodium dialkyl phosphites, or phosphorus trichloride in the presence of aluminium chloride, and also the addition of simple phosphorus derivatives to unsaturated compounds at multiple bonds.

Unsaturated compounds of the above types can be synthesised by these methods and also by such procedures as the addition of phosphorus pentachloride at multiple bonds with subsequent elimination of hydrogen chloride, the rearrangement of prop-2-ynyl phosphites, etc.

Interaction of ethynylmagnesium bromide in tetrahydrofuran with halogenated phosphorus derivatives has been used for the synthesis of phosphonous and phosphonic esters containing a terminal acetylenic group attached to the phosphorus atom. Dibutyl phosphorochloridite gives dibutyl ethynylphosphonite, which is hydrolysed to the corresponding acid ester[40-43]. By the use of dialkyl phosphorochloridates and phosphorofluoridates a few ethynylphosphonic esters have been obtained in low yields and in not entirely pure form[56,57]:

$$(C_4H_9O)_2PCl + BrMgC{\equiv}CH \rightarrow (C_4H_9O)_2PC{\equiv}CH \xrightarrow{H_2O} C_4H_9OP(H)(O)C{\equiv}CH.$$

$$(RO)_2P(O)X + BrMgC{\equiv}CH \rightarrow (RO)_2P(O)C{\equiv}CH$$

Examples have been given of the application of organomagnesium compounds to the synthesis of unsaturated phosphonites and phosphonates. This route proved inconvenient for the preparation of phosphonous and phosphonic acids, owing to experimental difficulties in the isolation of the final products and to the poor mobility of halogen in phosphorohalidates.

Reaction of phosphorus pentachloride with 1,3-diene hydrocarbons yields addition products, which can be converted into chlorides of the corresponding phosphonic, phosphonothionic, and phosphonoselenonic acids[68,77-80]:

$$CH_2{=}CHCH{=}CH_2 + 2\,PCl_5 \rightarrow ClCH_2CH{=}CHCH_2PCl_4{\cdot}PCl_5 \xrightarrow{H_2X} \longrightarrow ClCH_2CH{=}CHCH_2P(X)Cl_2 \xrightarrow[NR_3]{} CH_2{=}CHCH{=}CHP(X)Cl_2.$$

These acid chlorides can be obtained from alkenyne hydrocarbons and phosphorus pentachloride directly in one stage[69-76,81-85]. These hydrocarbons add the pentachloride at the triple bond[71,81,82]:

$$CH_2{=}CHC{\equiv}CR + 2\,PCl_5 \rightarrow CH_2{=}\underset{Cl}{C}H{-}\underset{R}{C}{=}CPCl_4{\cdot}PCl_5 \xrightarrow{SO_2} CH_2{=}\underset{Cl}{C}H{-}\underset{R}{C}{=}POCl_2 + POCl_3.$$

In the case of hydrocarbons containing a monosubstituted acetylenic group, however, the products of this reaction either add further a molecule of hydrogen chloride (with butenyne) or replace by chlorine a hydrogen atom in the saturated radical[71,72,81-83].

Shostakovskii, Guseinov, and their coworkers have published a series of papers on the addition of phosphorus pentachloride to alkoxy- and alkylthio-alkenynes[69,70,73-76,84,85]. The latest paper of this series[70] gives a more precise structure for the products, and shows that the reaction is represented by the equation

$$ROCH{=}CHC{\equiv}CH \xrightarrow[2.\ SO_2]{1.\ PCl_5} ROCH{=}CHCCl{=}CHPOCl_2.$$

The chlorides of phosphonic acids obtained by addition of phosphorus pentachloride to alkenynes have been converted by the usual methods into the corresponding esters, thio-esters, and amides.

Chlorides of phosphonic acids containing 1,3-diene substituents have been obtained also by the oxidative phosphorylation of butenyne, but the yields are low[86]:

$$CH_2{=}CHC{\equiv}CH + 2PCl_3 + O_2 \rightarrow CH_2{=}CHCCl{=}CH{-}POCl_2 + POCl_3.$$

Acetylenic hydrocarbons and phosphorus pentachloride have been used to obtain phosphonic acids and esters containing arylacetylenic substituents attached to the phosphorus atom. The chlorostyrylphosphonic chlorides formed initially were converted into the free acids[54] or the esters[66], and then dehydrochlorinated. Arylethynylphosphonic acids[55] and also 4-phenylbutadienylphosphonic acid[87] have been prepared for the first time by this method:

$$RC{\equiv}CH + PCl_3 \rightarrow RCCl{=}CHPOCl_2 \rightarrow RCCl{=}CHP(O)(OR')_2 \rightarrow RC{\equiv}CP(O)(OR')_2.$$

However, this is not a general path for the preparation of acetylenic phosphonates. When β-chloro-p-methoxystyrylphosphonic acid is used, for example, dehydrochlorination cannot be effected: the phosphorus–carbon bond undergoes fission[54].

The most fruitful reaction for the preparation of acetylenic phosphonates is the Arbuzov rearrangement. Early attempts to apply this process to halides of the prop-2-ynyl type containing a monosubstituted acetylenic bond resulted in the formation merely of isomeric compounds containing an acetylenic group attached to the phosphorus atom (in the case of prop-2-ynyl bromide[59]) or an allenic group[93]. This occurred also when a sodium dialkyl phosphite was used instead of the tertiary phosphite[59]. With prop-2-ynyl bromides having a disubstituted acetylenic group the "normal" Arbuzov rearrangement products were formed[61,64].

Halogenoacetylenes containing the halogen atom adjacent to the triple bond can also undergo the Arbuzov rearrangement with trialkyl phosphites, with formation of the normal products[65]. The most reactive compounds are those in which the triple bond is linked with another multiple bond, a benzene ring, or an electron-acceptor substituent such as a chlorine atom[58,64,67]. With respect to their reactivity the halogenoacetylenes are arranged in the series R–F > > R–Cl > R–Br > R–I, which is due to the diminution in polarisation of the ≡C–X bond in this sequence. Rearrangement involving halogenated acetylenes most probably takes place by the usual mechanism with the formation of a quasi-phosphonium compound as intermediate:

$$RC{\equiv}CX + P(OR')_3 \rightarrow RC{\equiv}CP(OR')_3X \rightarrow RC{\equiv}CP(O)(OR')_2 + R'X.$$

Phosphonic esters containing phenylethynyl, butenynyl, and butadiynyl substituents attached to the phosphorus atom have been obtained by this method, and several of them have been converted into the corresponding acid chlorides by the action of phosphorus pentachloride[68]. Dichloroacetylene gives with a phosphite under the same conditions diethyl chloroethynylphosphonate and bisdiethoxyphosphinylacetylene[58]. Use of monofluoroacetylene yields an ethynylphosphonic ester containing a terminal acetylenic group[58].

Phosphonic esters containing alkylethynyl substituents could not be obtained by the Arbuzov rearrangement[58,67]. Roundabout methods have been suggested for the synthesis of compounds of this type. Prop-1-ynylphosphonic ester is formed in low yield in the interaction of prop-2-ynyl bromide with triethyl phosphite[59] or sodium diethyl phosphite[64]. A more convenient method for the preparation of prop-1-ynylphosphonates is the reaction of dichloroacetone with two moles of triethyl phosphite, followed by treatment with sodium ethoxide[59]:

$$ClCH_2{-}CO{-}CH_2Cl \xrightarrow{P(OC_2H_5)_3} CH_2{=}\underset{O{-}PO(OC_2H_5)_2}{C}{-}CH_2Cl \xrightarrow{P(OC_2H_5)_3} \longrightarrow CH_2{=}\underset{O{-}P(O)(OC_2H_5)_2}{C}{-}CH_2{-}P(O)(OC_2H_5)_2 \xrightarrow{C_2H_5ONa} CH_3{-}C{\equiv}C{-}P(O)(OC_2H_5)_2$$

and also prototropic isomerisation of esters containing allenic substituents attached to the phosphorus atom[61], which can be conducted with or without isolation of the intermediate allenic compound[62,63,88]:

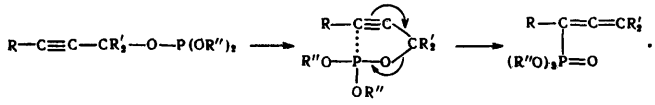
$$(RO)_2POCH_2{-}C{\equiv}CH \rightarrow CH_2{=}C{=}CHP(O)(OR)_2 \rightarrow CH_3C{\equiv}CP(O)(OR)_2.$$

The latter is not a general method, since, when homologues are used, the prototropic isomerisation either goes in a different direction or does not occur at all[61,63].

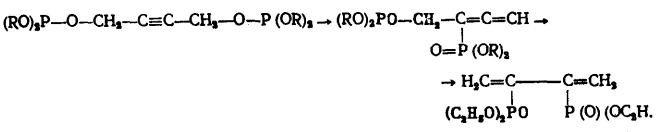
A process which is probably suitable for the preparation of various homologues of alkynylphosphonic acids has been employed for the synthesis of a but-1-ynylphosphonate[58]:

$$C_2H_5MgBr + ClC{\equiv}CP(O)(OC_2H_5)_2 \rightarrow C_2H_5C{\equiv}CP(O)(OC_2H_5)_2.$$

As stated above, esters formed by acids containing tervalent phosphorus with alcohols of the prop-2-ynyl type readily isomerise to give compounds containing an allenic group adjacent to the phosphorus[51,52,61-63]. Pudovik and his coworkers[88,89] have been able to show, by special investigations using mixtures of prop-2-ynyl phosphites, that this reaction involves intramolecular isomerisation with formation of an intermediate five-membered ring:



This reaction, which is in essence a variety of the Arbuzov rearrangement accompanied by acetylene–allene isomerisation, has made available various compounds containing an allenic group attached to phosphorus. Acetylenic glycols yield, together with allenic compounds, 1,3-diene-phosphonates containing two phosphinyl groups[51,90,91]:



In the case of prop-2-ynyl alcohol, as already stated, the reaction may not halt at the stage of the allenic compound. Available data on the synthesis of an allenic phosphonate by bromination and dehydrobromination of an allyl compound[92] require verification.

Physical constants of phosphonous and phosphonic acids containing acetylenic and diene substituents, and also of their functional derivatives involving the phosphorus, are given in Table 1.

Unsaturated phosphonous and phosphonic acids undergo reactions involving the phosphorus atom which are characteristic of their saturated analogues. Phosphonic esters containing acetylenic substituents react with phosphorus pentachloride to form chlorides of the corresponding acetylenic acids[68], which possess properties characteristic of the chlorides of saturated phosphonic acids. Their alcoholysis in the presence of triethylamine and their amidation at the phosphinyl group have been described[68,70,73-76,85].

Nucleophilic reagents add readily at multiple bonds in phosphonic esters of the present type, either one or two molecules being taken up with formation of a vinyl or a saturated derivative respectively[94,95].

Allenic phosphonates add at the double bond adjacent to the phosphorus atom[96]. Such nucleophilic reagents as dialkyl phosphites, thiols, secondary amines and alcohols add readily at multiple bonds in diene phosphinic esters in the presence of basic catalysts. Esters of acids containing 1,3-diene substituents add predominantly in the 1,4-positions[97].

Diels–Alder reactions have been reported in which butadiene-phosphonic and butadiene-phosphonothioic esters act as diene components[98]. References have been made in patents to the possibility of polymerising butadiene-phosphonic esters in the presence of benzoyl peroxide[78]. Finally, mention must be made of an interesting case of fission of the P–C≡ bond in an attempt to add alcohol to a prop-1-ynylphosphonic ester, a phosphoric ester being formed[95].

We conclude this review of methods of synthesis and chemical properties by noting that a few esters have been described formed by acetylenic alcohols with phosphoric and phosphonic acids[99-103]. Methods of synthesising these compounds do not differ fundamentally from those used for the saturated analogues. Work on the preparation of esters formed by prop-2-ynyl alcohols with acids containing tervalent phosphorus[104-106] require verification, since in fact the compounds obtained obviously have a different structure[51,52,62,107].

III. ELECTRONIC INTERACTIONS IN ORGANOPHOSPHORUS COMPOUNDS CONTAINING ACETYLENIC AND DIENE SUBSTITUENTS

The possibility of the conjugation of phosphorus with aromatic substituents and with a double bond has been discussed repeatedly in the literature. Most authors conclude that the four-coordinated phosphorus atom is only slightly involved in conjugation[11-13,108-110]. Little work has yet been done on the conjugation of phosphorus with a triple bond or on the effect of phosphorus on extended highly unsaturated systems.

A paper on the synthesis of phosphacyclopentadienyl compounds[39] has discussed the aromatic character of these structures. Pentaphenylphosphole[36-39] displays chemical properties characteristic of non-aromatic diene systems, which suggests that the phosphorus electrons are not involved in an aromatic sextet, in contrast to the position with pyrrole, which possesses appreciable aromatic character.

The situation is similar in open-chain highly unsaturated systems in which a phosphorus atom is attached to acetylenic or alkenyne substituents. Here, too, conjugation is far more evident in the substituent itself than between this substituent and the phosphorus atom. This is indicated in particular by the surprising constancy of the infrared frequencies of a triple bond attached to a phosphorus atom, these being practically independent either of the valency state of the phosphorus atom or of the nature of other substituents attached to this atom and being determined mainly by the structure of the acetylenic substituent. The C≡C and ≡C–H stretching frequencies in organophosphorus compounds containing a terminal acetylenic group lie within the ranges 2040–2090 and 3165–3300 cm^{-1} respectively[27,28,30,51,52,56-58,60]. It is interesting that these frequencies are appreciably higher (2120 and 3318 cm^{-1}) in the phosphine $(n\text{-}C_4H_9)_2PCH_2CH_2C{\equiv}CH$.[35] The C≡C stretching frequencies are determined in the case of a disubstituted triple bond by the structure of the acetylenic substituent: they are usually lower, within the range 2080–2180 cm^{-1}, for triple bonds conjugated with a benzene ring through a multiple bond or with a substituent containing lone pairs of electrons[27,28,30-35,47,48,53,58,61,64,65,67,68,111].

Unconjugated triple bonds linked to phosphorus, as also both conjugated and unconjugated triple bonds remote from the phosphorus, usually have frequencies lying in the range 2200 cm^{-1} and above[30,47,48,59-62,67] (but see Ref. 27). Phosphonates containing alkadiyne substituents exhibit two bands

due to the triple bonds, the frequency of the triple bond linked to the phosphorus atom being depressed[67].

The infrared spectra of derivatives of phosphonic acids containing 1,3-diene substituents attached to the phosphorus atom also contain two bands. The stretching frequencies of the double bonds lie in the usual range (1540–1640 cm^{-1}). The frequencies of allenic groups adjacent to the phosphorus atom lie within the usual limits (1925–1965 and 862–867 cm^{-1})[34,35,51,52,61]. The phosphoryl group in unsaturated compounds shows frequencies differing little from those in saturated compounds[112], which also indicates the insignificance of conjugation between this group and the multiple bonds.

Although the usual $\pi-\pi$ conjugation in highly unsaturated organic systems is greater in magnitude than conjugation of the phosphorus with the $\pi-\pi$ systems, the presence of the latter is suggested by the dipole moments (Table 2). This follows in particular from the considerable dipole moments of acetylenic and especially conjugated acetylenic phosphonates[65,113].

Published proton nuclear magnetic resonance data for organic phosphorus compounds containing one unsaturated substituent attached to the phosphorus atom do not permit us to assess the presence of conjugation with the phosphorus atom. It is true that the signal due to the acetylenic proton occurs at a lower field in ethynyldiphenylphosphine than in ethynyldialkylphosphines, and this has been taken to suggest the presence of conjugation[30], but it can equally be explained by the inductive effect of aromatic substituents, especially as the same paper mentioned a similar shift in the signal on passing from phosphines to phosphine oxides, under the influence of the strongly electronegative P=O group[30].

The chemical shifts and spin–spin coupling constants $J_{P,H}$ for protons separated from the phosphorus atom by more than one carbon–carbon bond (some of which may be unsaturated) vary in conformity with general views emerging from the study of other classes of compounds. Thus, for example, the accumulation of triple bonds in a substituent attached to the phosphorus atom displaces the terminal proton signal towards strong fields. This effect is explained by the diamagnetic anisotropy of triple bonds[30].

Oxidation and the addition of sulphur to acetylenic phosphines produce a sharp increase in the coupling constant $J_{P,H}$, owing to the increased electronegativity of the phosphorus atom[30].

With increase in the number of triple bonds the value of $J_{P,H}$ for the protons in the terminal methyl group decreases as a result of the increasing distance between the interacting nuclei. The decrease in $J_{P,H}$ is in general inversely proportional to the cube of the distance between the phosphorus nucleus and the proton, and a direct dipole–dipole mechanism has been suggested for this interaction[67].

In the case of phosphines an acetylenic proton is more strongly cleaved from the phosphorus through two triple bonds than through one triple bond (1.45 and 0.5 c/s respectively). This interesting fact has not yet been explained[30].

In the phosphorus nuclear magnetic resonance spectra[31] the chemical shift of the phosphorus nucleus in a diethoxyphosphinyl group adjacent to a triple bond has a constant magnitude of about +9 ppm (relative to 85% H_3PO_4). The small difference in the chemical shifts of acetylenic phosphonates having the triple bond in the $\alpha\beta$- and $\beta\gamma$-positions with respect to the phosphorus atom (29 ppm) has been interpreted as evidence of weak conjugation between the phosphinyl group and the triple bond[64].

TABLE 2. Dipole moments of diethyl esters of unsaturated phosphonic acids.

Compound	μ, D
$CH_2=CHCH_2PO(OC_2H_5)_2$	2.86
$CH_2CH=CHPO(OC_2H_5)_2$	2.92
$C_6H_5CH=CHPO(OC_2H_5)_2$	3.68
$CH_3C\equiv CPO(OC_2H_5)_2$	3.94
$CH_2=C(CH_3)C\equiv CPO(OC_2H_5)_2$	3.84
$CH_2=CHC\equiv CPO(OC_2H_5)_2$	3.88
$CH_3CH=CHC\equiv CPO(OC_2H_5)_2$	4.06
$C_6H_5C\equiv CPO(OC_2H_5)_2$	4.17
$C_6H_5C\equiv CC\equiv CPO(OC_2H_5)_2$	4.39

Thus to the extent that it is possible at all to assess the electronic interaction between phosphorus and unsaturated systems by the methods used to judge $\pi-\pi$ conjugation[11–13], it must be concluded that phosphorus is less well conjugated with a $\pi-\pi$-conjugated substituent than is the substituent itself conjugated. Nevertheless, conjugation of a triple bond with phosphorus-containing groups is rather better than is that of a double bond[111].

A second interesting group within the class of compounds under discussion comprises those containing three unsaturated substituents attached to the phosphorus atom, their structure being close to tetrahedral. Cruickshank has shown[114] that strong $\pi-d$ bonding can be assumed in tetrahedral ions of the type XO_4^{n-} (where X = P, S, Cl), owing to the effective overlapping of two of the five vacant d-orbitals of the central atom ($d_{x^2-y^2}$ and d_{z^2}) with eight non-bonding $2p\pi$-orbitals of the oxygen atoms (two orthogonal orbitals on each atom). Apart from the appropriate symmetry of these orbitals, interaction is ensured by the decrease in their energy and increase in the magnitude of the overlap integrals[115,116] due to the presence of the positive charge on the central atom.

A definite analogy can be traced between tetrahedral ions and tertiary phosphine sulphides having three acetylenic substituents attached to the phosphorus atom. In fact each of the triple bonds has two orthogonal π-orbitals, and the datively bound sulphur atom has two orthogonal p-orbitals. It is true that, in view of the presence of the datively bound sulphur, tertiary phosphine sulphides should have had dipole moments of the order of 10 D (transfer of one electron along the bond), whereas actually their moments do not reach half this value. But this fact is immediately explained by $p-d$ interaction between the sulphur and the phosphorus[117].

The present Reviewers have studied the dipole moments and the ultraviolet, infrared, and ^1H-nuclear magnetic resonance spectra of a series of sulphides of unsaturated tertiary phosphines[47–49]. The long-wavelength band in the ultraviolet spectra undergoes a bathochromic shift as unsaturated substituents accumulate at the phosphorus atom, the absorption intensity changing disproportionately to the number of unsaturated substituents (Table 3). This fact has been interpreted as confirming conjugation of the unsaturated substituents with the central phosphorus atom.

It has been mentioned above that the frequency of the triple bond in the infrared spectra of sulphides of tertiary acetylenic phosphines is practically independent of the

TABLE 3. Ultraviolet spectra of sulphides of unsaturated tertiary phosphines.

Compound	λ_{max}, nm	$10^{-3}\epsilon_{max}$
$(CH_3)_2P(S)C{\equiv}CCH_3$	221	4.34
$CH_3P(S)(C{\equiv}CCH_3)_2$	234	3.38
$P(S)(C{\equiv}CCH_3)_3$	250	4.46
$(CH_3)_2P(S)C{\equiv}CC_6H_5$	246	20.50
$CH_3P(S)(C{\equiv}CC_6H_5)_2$	253	38.45
$P(S)(C{\equiv}CC_6H_5)_3$	256	49.13
$(C_6H_5)_2P(S)CH{=}CHC_6H_5$	264	29.89
$C_6H_5P(S)(CH{=}CHC_6H_5)_2$	267	47.24
$P(S)(CH{=}CHC_6H_5)_2$	277	46.12

number of acetylenic substituents attached to the phosphorus atom. Study of the ^1H-nuclear magnetic resonance spectra of these compounds shows that this does not imply the absence of transmission of electron interactions through the phosphorus atom[48]. Table 4 gives the chemical shifts and spin–spin interaction constants for the protons in methyl groups combined with the phosphorus atom [40 Mc/s, 10 mole % in CCl_4 and $(CH_3)_4Si$, internal standard].

As acetylenic substituents accumulate at the phosphorus atom, and also with increase in their electron-acceptor properties, the spin–spin interaction constant with the phosphorus nucleus increases, while the chemical shift of the protons decreases. With the protons of methyl groups adjacent to the triple bond, however, the usual dependence of the chemical shift on the electron-acceptor properties of the substituents breaks down[53] (Table 4). Firstly it must be noted that the chemical shift of the protons of methyl groups in prop-1-ynyl substituents is of the same order of magnitude as the chemical shifts of protons in methyl groups directly attached to the phosphorus atom, although the signal due to the former should have been located in the region of smaller fields (in view of the greater electron-attracting power of the triple bond). Furthermore, as triple bonds accumulate at the phosphorus atom the shift due to protons of methyl groups adjacent to a triple bond should still have been displaced to smaller fields, whereas actually it is raised (Table 4).

The results obtained can be explained by the superposition of three effects: on the one hand, there is actually a diminution in electron density under the influence of electronegative substituents, while on the other hand the protons are magnetically screened by the diamagnetic anisotropy of the triple bond, which to some extent balances the electronegativity effect. Finally, perhaps, the accumulation of identical acetylenic substituents at the phosphorus atom is accompanied by a decrease in the paramagnetic contribution of the phosphorus to the anisotropy owing to the enhanced symmetry of the molecule, which results in an additional increase in screening. As a result, maximum sphericity of the electron cloud of the molecule is achieved on passing to a trialkynyl derivative as a consequence of the maximum utilisation of the *d*-orbitals, and the proton chemical shift increases sharply. The spin–spin coupling constant increases in the same sequence as in the previous case, while its magnitude is appreciably less owing to the increase in distance between the protons and the phosphorus nucleus, which corresponds to general views on the way in which it varies.

A similar conclusion concerning the possibility of conjugation with the phosphorus atom in tetrahedral molecules of the sulphides of unsaturated tertiary phosphines is reached from a study of the dipole moments of these compounds[49]. Comparison of the dipole moments of tertiary phosphines and phosphine sulphides containing phenyl- and *p*-tolyl-ethynyl groups indicates that the vector of the resultant moment is directed from the acetylenic substituents towards the phosphorus atom. With the moment in this direction, it would be expected to decrease with increase in the electron-attracting power of the substituents. This is in fact observed in the halides of three-coordinated phosphorus, tertiary acetylenic phosphines, and also thiophosphoryl halides. In the case of the sulphides of tertiary acetylenic phosphines, however, an appreciable increase is observed in the dipole moments with increase in the sum of the inductive constants [σ^*-values] of the substituents attached to the phosphorus atom [Table 5]. This increase can be explained by the presence of some positive electronic effect acting in the same direction as the vector representing the overall moment of the molecule. The effect may be caused by the presence of moments due to the substituents themselves, the contribution of which to the total moment of the molecule will increase with increase in the number of these substituents. On the other hand, it can be explained by π–*d* interaction between the acetylenic substituents or the halogens and the phosphorus atom, this increasing with increase in the number of these substituents from 1 to 3, when maximum effective utilisation of the *d*-orbitals becomes possible: i.e. it increases in parallel with the dipole moment. In the sulphides of acetylenic phosphines, accumulation of acetylenic substituents is accompanied by a more rapid increase in π–π interaction than in the negative inductive effect of the substituents, and a general increase in dipole moment is observed. In the thiophosphoryl halides, in contrast, the negative effect increases more rapidly (as halogen atoms accumulate), and a general decrease in dipole moments is observed[53].

Published data indicate that the conjugation of phosphorus with highly unsaturated π–π systems is less marked than conjugation within the π–π systems themselves.

TABLE 4. Chemical shifts and spin–spin interaction constants of protons forming methyl groups in sulphides of acetylenic phosphines.

Compound	σ_{CH_3}, ppm	$J_{CH_3,P}$, c/s	$\sigma_{C\,|\,CCH_3}$, ppm	$J_{C\,|\,CCH_3,P}$, c/s
$(CH_3)_2P(S)C{\equiv}CCH{=}CH_2$	−1.9	12.9	—	—
$(CH_3)_2P(S)C{\equiv}CCH_3$	−1.9	13.5	−2.2	2.4
$CH_3P(S)(C{\equiv}CCH_3)_2$	−2.0	14.4	−2.1	4.1
$P(S)(C{\equiv}CCH_3)_3$	—	—	−1.0	4.7
$(CH_3)_2P(S)C{\equiv}CC_6H_5$	−2.0	15.0	—	—
$CH_3P(S)(C{\equiv}CC_6H_5)_2$	−2.2	16.0	—	—

TABLE 5. Dipole moments of sulphides of acetylenic phosphines.[49]

Compound	$\Sigma\sigma^*$	μ, D
$(p\text{-}CH_3C_6H_4C{\equiv}C)_3PS$	+3.99	5.47
$(C_6H_5C{\equiv}C)_3PS$	+4.05	5.32
$(CH_3C{\equiv}C)_3PS$	+3.90	5.20
$C_6H_5P(S)(C{\equiv}CC_6H_5)_2$	+3.30	5.20
$CH_3P(S)(C{\equiv}CC_6H_5)_2$	+2.70	5.14
$C_6H_5CH{=}CHP(S)(C{\equiv}CC_6H_5)_2$	+3.11	5.12
$(CH_3)_2P(S)C{\equiv}CC_6H_5$	+1.35	4.91
$(CH_3)_2P(S)C{\equiv}CCH_3$	+1.30	4.90
$(CH_3)_2P(S)C_2H_5$	−0.10	4.66

Furthermore, the phosphorus may be involved in conjugation with unsaturated substituents arranged tetrahedrally about the phosphorus atom, and, although this conjugation is small, it can be detected by physical methods. However, the possibility of fundamentally different explanations of the behaviour of organophosphorus compounds must be borne in mind.

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THE WOLFF REARRANGEMENT

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CONTENTS

I. Introduction 260
II. Definition and mechanism of the Wolff rearrangement 261
III. Stereochemistry of the Wolff rearrangement 263
IV. Chief synthetic applications of the Wolff rearrangement 264
1. Wolff rearrangement as a method of synthesising homologous acids 264
2. Wolff rearrangement as a method of ring contraction 266
V. Reactions competing with the Wolff rearrangement 267
1. Hydrogen and alkyl migration 267
2. Dimerisation and trimerisation 268
3. Formation of ketazines 268
4. Oxidation of intermediate carbenones 268
5. Intramolecular addition of carbenones at a double bond 269

I. INTRODUCTION

The great reactivity and comparatively ready accessibility of α-diazo-ketones have contributed to the rapid development of the chemistry of this peculiar class of organic compounds — see the most important reviews[1-11].