The Michaelis–Arbuzov Rearrangement

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I. Introduction

The Michaelis–Arbuzov rearrangement, also known as the Arbuzov rearrangement, Arbuzov reaction, or Arbuzov transformation, is one of the most versatile pathways for the formation of carbon–phosphorus bonds and involves the reaction of an ester of trivalent phosphorus with alkyl halides. The reaction, originally discovered by Michaelis[1] in 1898, was explored in great detail by Arbuzov[2] and several subsequent investigators. The rearrangement is one of the most thoroughly investigated among organophosphorus reactions and is widely employed for the synthesis of phosphonates, phosphinic acid esters, and phosphine oxides.

In its simplest form the Arbuzov arrangement is the reaction of an alkyl halide with a trialkyl phosphite, yielding a dialkyl alkylphosphonate (1). Thus, during

$$(RO)_3P \ + \ R'{-}hal \ \xrightarrow{\triangle} \ R'{-}\overset{\displaystyle O}{\underset{\displaystyle OR}{\overset{\|}{P}}}{-}OR \ + \ R{-}hal$$

1
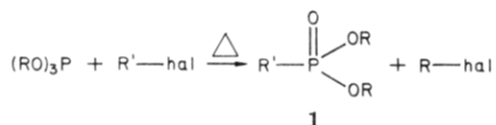
R = alkyl, aryl, etc.
R¹ = alkyl, acyl, etc.
hal = Cl, Br, I

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the transformation a tervalent phosphorus (P_{III}) is converted into a pentavalent phosphorus (P_V). In general, the alkyl group of the halide gets attached to the phosphorus, and one alkyl from phosphorus combines with halogen to form the new alkyl halide.

The rearrangement has been discussed in a book on organophosphorus compounds[3] and in two reviews[4,5] dating back to 1964. To date there is no available review of the subject in English, though several have

appeared in German[5,6] and Russian.[7] The present effort, which covers the literature through December 1978, is aimed at providing more recent information on the topic. The subject matter includes the mechanism, scope of the reaction, synthesis of different kinds of organophosphorus compounds via rearrangement, recent modifications, i.e., the rearrangement of trialkyl phosphites in presence of nonhalogen compounds, behavior of sulfur and fluorine analogues under Arbuzov conditions, and also some discussion about anomalous Arbuzov reaction.

II. Reaction Mechanism

On the basis of numerous investigations[8-11] the following mechanism may be written for the rearrangement.


2
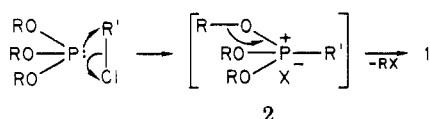
The lone pair of electrons of the phosphite attacks the alkyl group of the alkyl halide to form the addition compound 2 in which the alkyl group of the alkyl halide gets attached to the phosphorus. In the next step an alkyl group of the phosphite dissociates from 2, resulting in the formation of the P=O bond; the alkyl group is eliminated as the new alkyl halide. The overall result of the two steps is the conversion of trivalent phosphorus into pentavalent. When the alkyl groups of the phosphite and the alkyl halides are identical, i.e., R = R', the process amounts to an isomerization of the phosphite.

It is reported that the conversion of >P—O—C linkage into >P(=O)—C involves a net gain of 32-, and possibly 65-, kcal/mol energy in the total bond stability[12] and acts as a driving force for the rearrangement. However, an accessible path for the redistribution of electron density is also required to effect the conversion.

Haloalkyl phosphites undergo internal rearrangement on heating the halogen present in the phosphite itself acting as an alkyl halide. For example, tris(β-chloroethyl) phosphite (3)[13] undergoes isomerization to the phosphonate 4 on heating to about 150 °C.
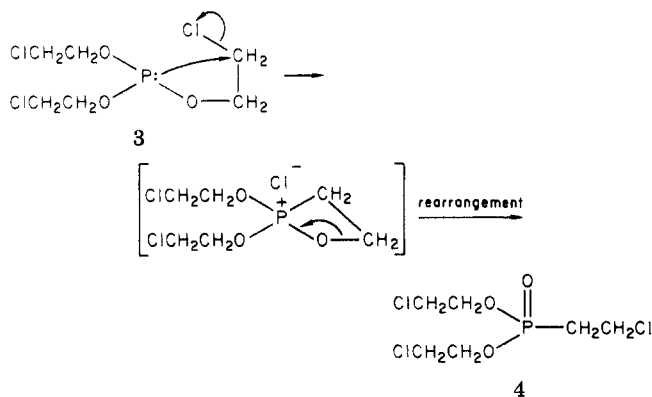

The Michaelis–Arbuzov reaction of phosphinite esters also proceeds by way of quasiphosphonium intermediates of the above type. Evidence for their formation is obtained by the isolation[14] of crystalline 5, mp 56–58 °C. A similar compound, 6, mp 79–81 °C, was also obtained from the reaction of the phosphorus ester with ethyl iodide. Storage of these products over P_2O_5 at

5   6
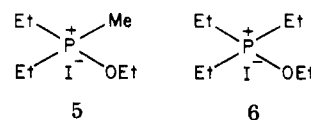
18–21 °C for 15–25 days resulted in their decomposition to the phosphine oxides.

In the case of alkyl esters, the phosphonium intermediate 2 cannot normally be isolated. However, by employing a methylating agent with a very weakly nucleophilic leaving group, e.g., methyl trifluoromethanesulfonate, the phosphonium salts with trialkyl phosphites also have been isolated.[15] A stable 1:1 intermediate, however, can be obtained in several instances from triaryl phosphites[16-20] and in other special cases involving triaryl phosphites and α,β-dihaloalkyl ethers. In the reaction of carbonium salts such as triphenylmethyl tetrafluoroborate the intermediate could also be obtained.[21,22] Tris(neopentyloxy) phosphite on mixing with methyl iodide in equimolar proportion at room temperature is also reported[23] to give a crystalline Michaelis–Arbuzov intermediate, 7, which decomposed
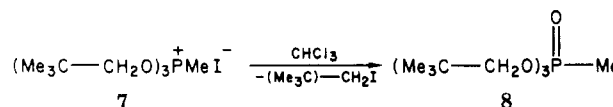
in chloroform in a first-order reaction to give the phosphonic acid diester 8.

Alkali alcoholates or sodium bicarbonate also causes cleavage of 7 to 8. In general the intermediates from triaryl phosphites and alkyl halides could be cleaved thermally (above 200 °C) or by reaction with alcohols or bases to give the phosphonates.[19]

In his classic work,[24] Arbuzov formulated the pentacoordinated compound as the intermediate in the rearrangement and gave structure 9 to the addition com-


9   10   11
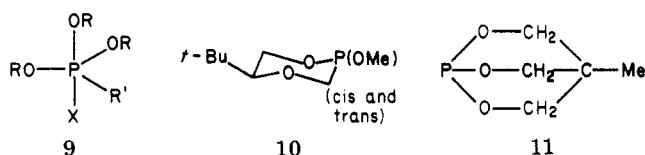
pound of phosphite and alkyl halide. Although a number of these addition products, in crystalline state, have been known for a long time, not much had been said by the earlier workers[4,23,25] about their structure except referring to them as "quasiphosphonium salts". The P–X bond in these compounds has been reported[16,20] to be partially ionic and partially covalent in nature. A phosphonium salt structure (2) is also very widely used for these products.

The mechanism of the reaction has been studied with a number of five- and six-membered-ring phosphites. These compounds exist in a mixture of cis and trans forms. It was observed that the five-membered cyclic phosphites could be oxidized stereospecifically by nitrogen tetroxide to the phosphates.[26] Similarly high stereoselectivity was also noted in reaction of six-membered-ring systems with halides[27] and free radicals.[27c] Thus a mixture of trans and cis phosphites 10 on reaction with CH_3I gave the methyl phosphonates in practically the same proportions.[27a] Similarly, ethylation of ethyl phenyl phosphinate via ethyl (trimethylsilyl)phenyl phosphonite and some allied systems also proceeds with almost complete retention of configuration.

The stereochemistry of the reaction has been used by different workers[29] to distinguish between two possible pathways. Thus Wadsworth and co-workers[29a] treated the six-membered cyclic phosphite system with various nucleophiles and observed that the outcome of the reaction was influenced by the basicity of the attacking nucleophile. In the above reaction the added cations also influenced the stereochemistry in a dramatic manner.[29b] Using the stereochemistry some workers have proposed that the first step in the reaction is the formation of an alkoxyphosphonium salt followed by dealkylation to the corresponding phosphoryl compound. Hudson and Brown[29d] attempted to explain the stereochemistry of the phosphorus heterocycles in the terms of the effect of ring strain.

The studies on the reaction of diasteroisomeric cyclic phosphites with alkyl halides revealed a lack of stereospecificity at phosphorus which was explained by the intermediacy of a pentacovalent intermediate.[30,31] Bodkin and Simpson have suggested[30] that in the "normal" Arbuzov reaction with alkyl halides, the pentacoordinate species 12 is formed initially and subsequently either dissociates into the phosphonium salt 13 or is dealkylated.

12

13
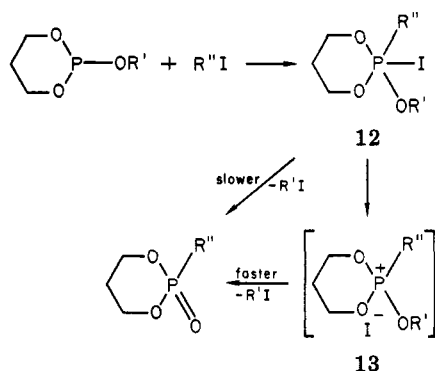
A ^{31}P NMR study of these compounds could give more insight into their structure as P(V) and P(IV)⁺ are known[32] to absorb at different fields. In recent studies[33,34] on sterically hindered phosphites, the intermediates have been actually isolated and characterized by ^{31}P NMR, which suggests a phosphonium structure for these intermediates. A phosphonium intermediate was also detected[35] in the bromination of 11. However, the authors[34] were of the view that the pentacovalent species could have been formed as a short-lived intermediate en route to the phosphonium structure.

More recently direct evidence by ^{31}P NMR spectrometry has been adduced[36] for the formation of a five-coordinate intermediate in the reaction of 14 with


14
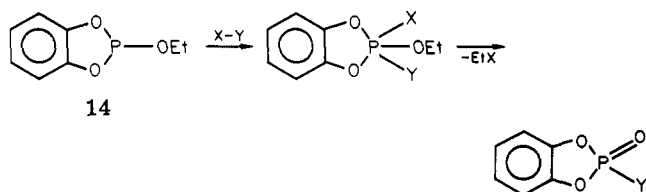
a, X = Y = Cl
b, X = Y = Br
c, X = Cl; Y = Ph

elemental chlorine, bromine, and benzenesulfenyl chloride. Studies on the stereochemistry of the deal-

kylation step show evidence for an equilibrium between phosphorane and phosphonium species.[37]

Decomposition of alkoxyphosphonium intermediates 2 resulted from the nucleophilic attack of X⁻ on R to form phosphoryl groups that provide the driving force for the P^{III} to P^{V} transformations. The importance of nucleophilicity of the negative ion in effecting the decomposition is further exemplified by the stability of alkoxyphosphonium hexachloroantimonates,[38] nitrates,[38] and tetrafluoroborates;[39] the anions of these salts are essentially nucleophilic.

The general mode of attack of R by X⁻ follows an S$_N$2 mechanism, X⁻ attacking from the back side with simultaneous O–R bond-breaking and R–X bond formation. This is supported by the observation[40] that in the decomposition of the alkoxyphosphonium salts 16, which are analogous to 15, inversion of configuration of the asymmetric carbon in 17 did occur.


15

16

17
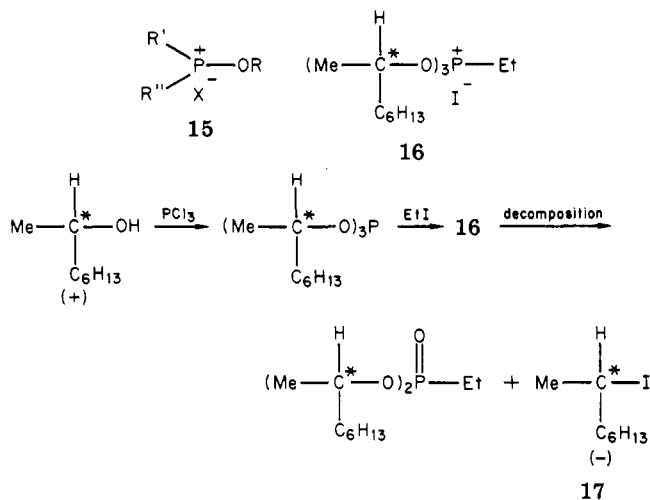
In conformity with the S$_N$2 mechanism, the reactivities of mixed trialkyl phosphites are known[16] to decrease with R in the order Me > Et > i-Pr. However, a carbonium ion mechanism can also operate during the decomposition step of the intermediate:[25,41] R first gets dissociated from the phosphonium salt and is then attacked by the X⁻. Support for this mechanism is provided by the phosphinite esters bearing tertiary alkyl substituents which also undergo the rearrangement[41,42] (eq 1). Thus both S$_N$2 and S$_N$1 mechanism are possible.

(1)
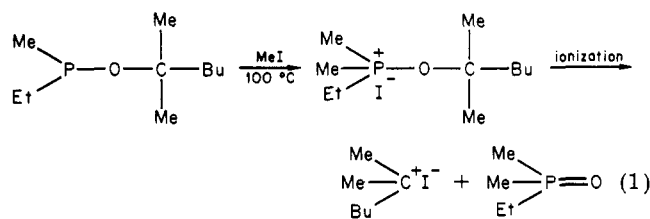
III. Scope and Limitation of the Reaction

The two reactants in the Arbuzov rearrangement are alkyl halide and trialkyl phosphite. In a general way the reaction may be written


18
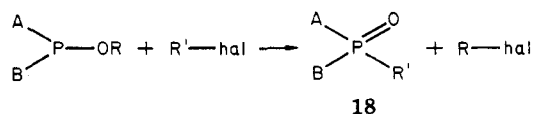
where A and B may be same or different alkoxy groups.

This enables a wide choice of phosphites as well as alkyl halides to bring about the formation of a carbon–phosphorus bond and makes the Arbuzov rearrangement a versatile synthetic tool. In some cases catalysts are useful, even necessary. Thus, the scope of the reaction is limited only by the availability of phosphites and alkyl halides and in applicable cases on the effectiveness of the catalysts used.

A. Alkyl Halides

It appears that any halide capable of reacting with nucleophilic reagents by an S_N2 mechanism and not containing any potentially interfering groups (such as carbonyl or nitro) is suitable for the reaction. Generally the reactivity of organic halides follows the sequence[43] RCO-hal > RCH_2-hal > R_2CH-hal $\gg$ RR'R''C-hal; RI > RBr > RCl.

Whereas the primary alkyl halides react normally, tertiary alkyl halides and simple aryl and vinyl halides are unreactive toward trialkyl phosphites, in conformity with their behavior toward S_N2 reactions. Benzyl, diphenylmethyl, and triphenylmethyl halides all give expected phosphonates,[44-46] as do halogenomethyl derivatives of condensed aromatic hydrocarbons;[47] e.g., with benzyl bromide[44b]

R = Et, Me$_2$CH, Pr, ClCH$_2$CH$_2$
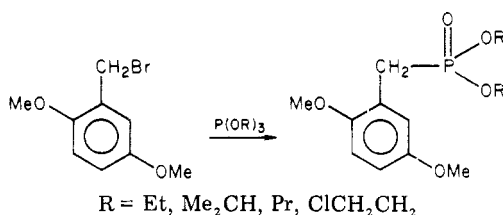
The aliphatic halides used have mostly been primary halides. Only a few secondary halides react satisfactorily, e.g., isopropyl iodide[48] and ethyl α-bromopropionate.[49] Generally the secondary and tertiary alkyl halides either fail to react or may decompose to give olefins.

In addition to alkyl halides other organic halides also react with trialkyl phosphites according to the Michaelis–Arbuzov scheme. Thus esters of 2-bromoethanol with aliphatic carboxylic acids,[50] halogen ethers, and acyl halides[51] react normally. Esters of α-monohalo monocarboxylic acids likewise give α-carboxyalkylphosphonates[52] (19).

$$\text{R'OOC—CH}_2\text{-hal} \xrightarrow[-\text{Rhal}]{\text{P(OR)}_3} \text{R'OOC-CH}_2\text{-PO(OR)}_2$$
$$\mathbf{19}$$
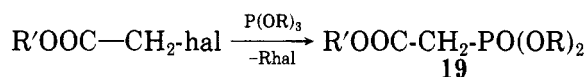
Isocyanide dichloride[53] and imidochlorides[54] may also be used in the reaction, the former reacting at room temperature to give carbonimidoylbisphosphonates (20).
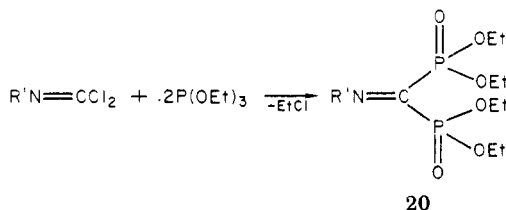

Chloroformic acid esters yield phosphonoformic acid esters.[55,56] Phosphonoformamide ester is obtained from carbamide acid chloride[57] whereas phosphonothioformamide ester is obtained from thiocarbamic chloride.[58]

Haloalkyl amide[59] and N,N-bis(haloalkyl)acrylamide (21)[60] also react according to eq 2; α-allyl halides (22)
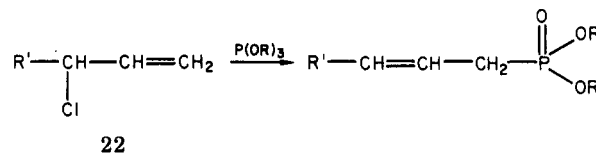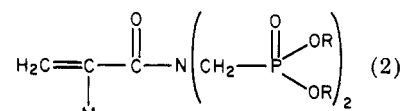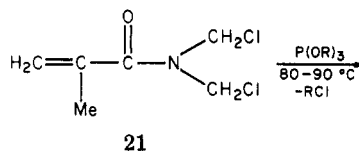
react with phosphites as expected;[61] and internal allyl halides may partially undergo allyl shifts.

Similarly, with 23 and 24 the expected phosphonates are obtained.[62]

R = Et
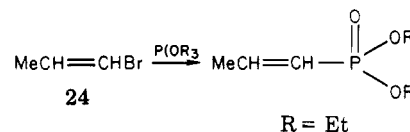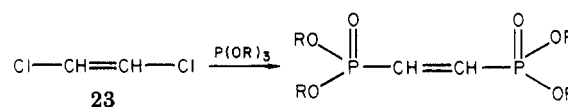
Propargyl halides (25) react[63] as in eq 3. 27 is further
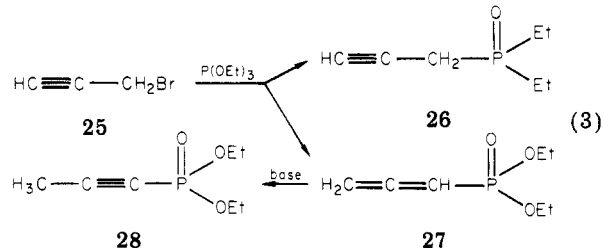
isomerized to 28 in the presence of bases.

Acyl chlorides react readily to form α-ketophosphonic acid esters. Maleic acid dichloride yields only tarry products. α-Halovinyl ketones and esters react to yield the corresponding phosphonic acid esters.[64] In an interesting variation, 2,2'-dichloro-2,2'-azopropane (29) also has been recently reported[65] to give an Arbuzov product.

60%
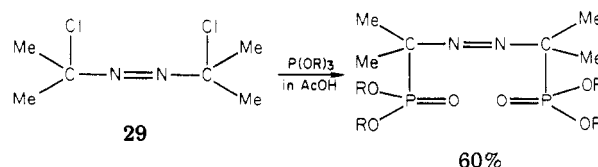
Saturated α-chloro/bromo ketones and aldehydes, however, give the normal Arbuzov product only as a minor product of the reaction. On reaction with trialkyl phosphites, the α-chloro/bromo carbonyl compounds are known to give a P–O bond rather than P–C bond. This mode of "anomalous reaction" is known as the Perkow reaction,[66] the products of the reaction being dialkyl vinyl phosphates. In this reaction also the first step, namely, the formation of the intermediate product,

is also the same as in Arbuzov reaction, involving nucleophilic attack of phosphorus on the carbon atom. The intermediate then "decomposes" to give the phosphate **30** formed by nucleophilic attack (on the phosphorus) by the carbonyl oxygen[67-69] followed by normal Arbuzov elimination of alkyl halide; consequently the normal phosphonate (**31**) is not obtained.

Arbuzov intermediate
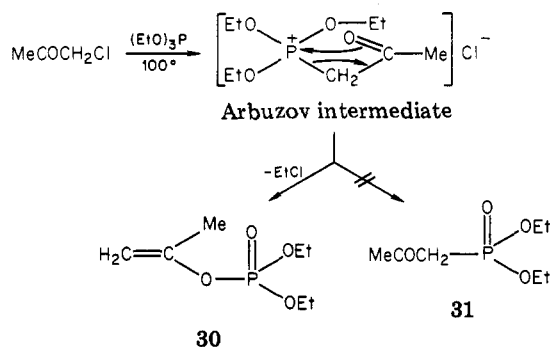
With α-chloro/bromo ketones both the normal and abnormal products are obtained; e.g., with substituted α-bromo acetophenone:[70-72] The yields of **33** decreased
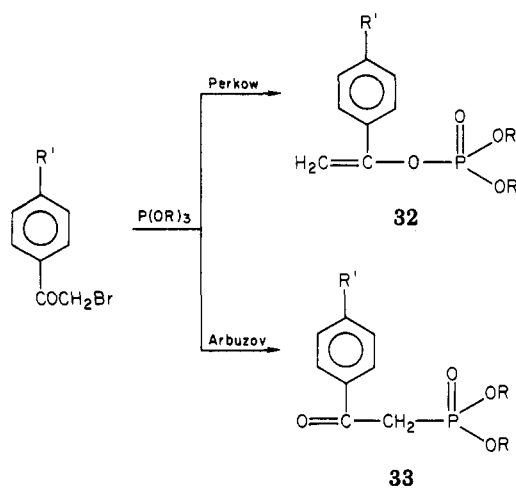
and **32** increased in the order R′ = MeO, Me, H, F, Cl, Br, NO₂.

However, α-iodo ketones give the normal phosphonates[73,74] (and not phosphate) as the main product of the reaction. The reason for this normal behavior is the lesser electronegativity of iodine exerting a smaller polarization effect as well as its greater reactivity toward simple displacement. Other chloro ketones and polyhalo ketones behave abnormally toward the Arbuzov reaction because of the polarization 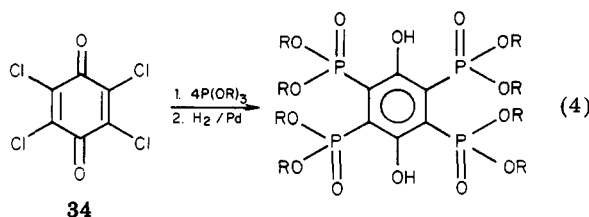induced on the carbonyl group by the electronegative halogen atoms. The formation of phosphonates is also favored by carrying out the reaction at higher temperatures.[73]

Chloranil (**34**) reacts in an interesting way with the trialkyl phosphite esters of secondary alcohols, as shown in eq 4.[75] Methylene and other dihalides react normally

but less readily, and depending on the ratio of the

reactants, one or both the halogens may be replaced.[76] Chloroform does not react with triethyl phosphite even under drastic conditions,[77] but carbon tetrachloride reacts surprisingly readily, though only one chlorine gets displaced.[78] This reaction is accelerated by UV irradiation or peroxides and proceeds via a free-radical mechanism.[79] However, CCl₄ is known to react with triethyl phosphite via both radical and nonradical pathways.[80] Interestingly, phosgene immonium chloride gives tris(alkylphosphonic acid) esters[81] (**35**).
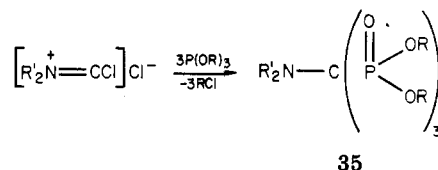
R = Et; R′₂N = Me₂N, N-morpholinyl

Earlier claims regarding the synthesis of methanetriphosphonic acid ester derivatives could not be verified by later experiments.[82,83]

Simple aryl halides are very unreactive toward the Arbuzov reaction. Iodobenzene is reported to react with trimethyl phosphite on photolysis at 60 °C to give the Arbuzov product **37** by a free-radical mechanism.[84] Ph· is the phenylating species in this reaction.
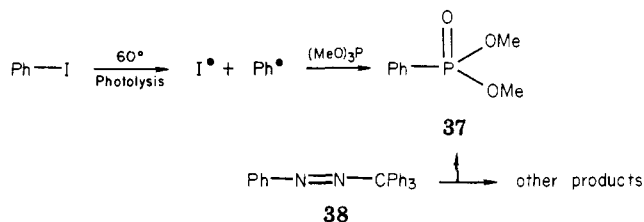
The decomposition products of (phenylazo)triphenylmethane (**38**) in trimethyl phosphite also yields **37**; here the yield of **37** is 96–99% of theoretically available phenyl radical.[85] Iodobenzenes have also been shown to react rapidly with potassium dialkyl phosphites in liquid ammonia under "350-nm" irradiation to give the Arbuzov product dialkyl arylphosphonates in about 90% yield.[86]
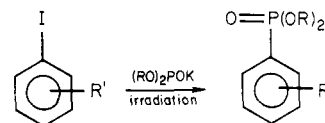
Activated aryl halides, especially those having heterocyclic nuclei such as acridine, thiazoles, quinoxaline, isoxazole, coumarin, and tetrahydrofuran systems, have been used.[87,88] 2,4-Dichloroquinazolines[89] (**39**, **40**) and **41** react preferentially at the 4-position.
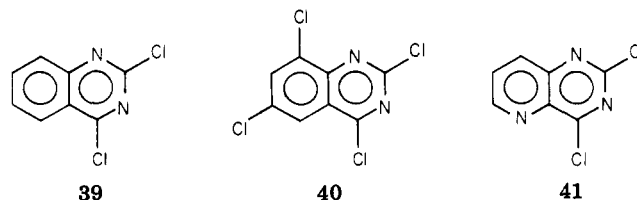
In **40**, the Cl atoms at C₂ and C₄ were replaced simultaneously by the incoming phosphonate group; i.e., a diphosphonate was obtained.

SCHEME I. Synthesis of Phosphonate, Phosphinate, and Phosphine Oxides
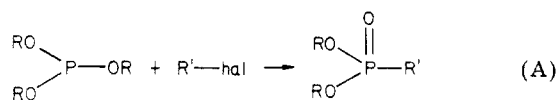
44 (phosphonate)
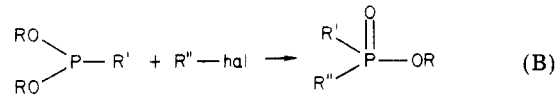
45 (phosphinate)
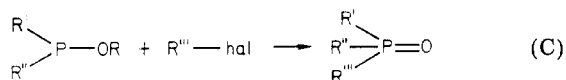
46 (phosphine oxide)

1-(Chloromethyl)-5,5-dimethylhydantoin (**42**) is reported[90] to react in the usual manner to give **43**.

B. Tricoordinate Phosphorus Reactant

The general structure of the phosphorus ester may be written as ABP–OR where A and B may be primary alkoxy, secondary alkoxy, aryloxy, alkyl, aryl, or dialkylamino groups. As the reaction involves nucleophilic attack of the unshared pair of electrons of the phosphorus on the alkyl halide, it is retarded if A, B are electron-attracting groups and accelerated if they are electron-repelling groups, the ease of reaction increasing in the order A, B = aryloxy < alkoxy < aryl < alkyl < dialkylamino.

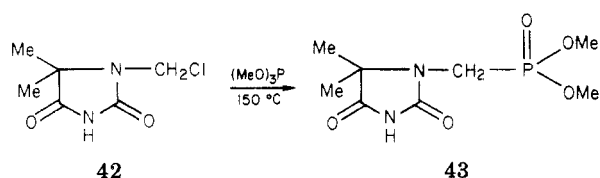The R should be aliphatic for the reaction to proceed smoothly. If A and B in the phosphite ABP–OR are alkoxy groups, then a phosphonate (**44**) is obtained; when one is alkoxy and the other is alkyl or aryl, then a phosphinate (**45**) is obtained. If both A and B are alkyl or aryl groups, then a tertiary phosphine oxide (**46**) is obtained on rearrangement (Scheme I). When R is alkyl, then in the reaction with CH_3I, the reactivity of mixed trialkyl phosphites decreases with R in the sequence[16] Me > Et > i-Pr. Triaryl phosphites do not undergo the Arbuzov rearrangement as such, though they isomerize on heating with alcohols at higher temperatures[91,1] (eq 5).
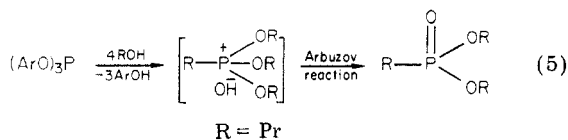
Cyclic phosphites of structure **47** and **48** generally
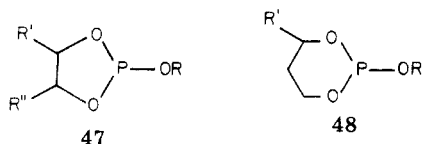
react[46] with alkyl halides with exchange of R. Compounds of structure **49**, however, undergo ring opening[46,92] to form **50** which upon heating gives rise to the ring by by cleavage of an alkyl halide.
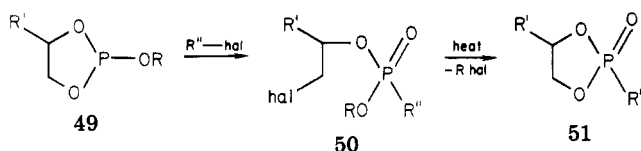
The dioxaphosphorinanes (**52**) react as in eq 6.
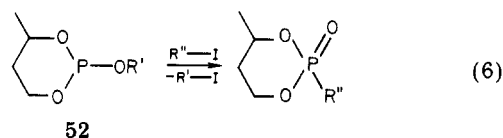
Of interest is also the reaction of diazaphospholines (**53**) which give the Arbuzov product **54** on reaction with alkyl halide.[93]
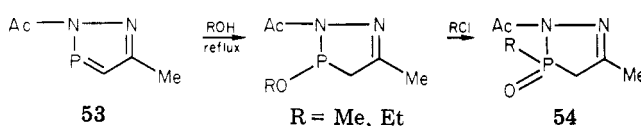
Similarly, 1-phospha-2,6,7-trioxabicyclo[2.2.2]octane (**11**) reacts with allyl halide to give an Arbuzov product (**55**).[34,35,94]
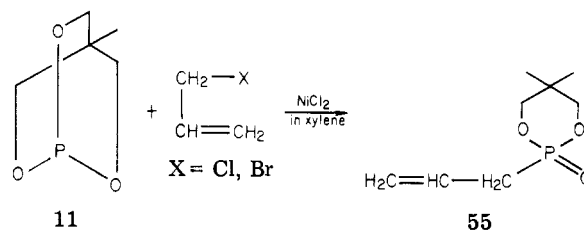
As only one alkoxy group of a phosphite participates in the reaction leading to phosphonates, it could be expected that partial esters of phosphorus acids and esters of amidophosphorus acids would react in the same way. These variations of the reaction were developed by Michaelis.[95,96]

The dialkyl acid phosphite salts also react quite satisfactorily in an Arbuzov-like manner; e.g., dibutyl 1-decanephosphonate (**57**)[97] is prepared from decyl bromide and **56** as in eq 7. (This reaction is somewhat
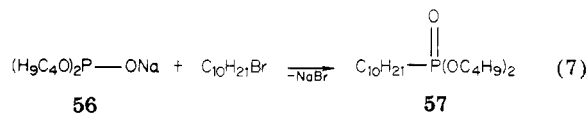
similar to the photochemical reaction of iodobenzene with dialkyl phosphite salts[86]).

The synthesis of the bis(diethylamide) of methanephosphonic acid (**58**)[96] provides an example of the use of amidophosphites.
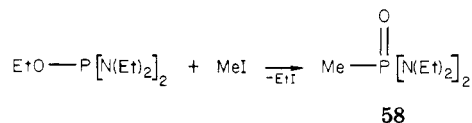
In the general category the reaction of methylol derivatives of acyl amides to give **59**[98] and the reaction of

RCONHCH₂OH $\xrightarrow[\text{−HCl}]{\text{PCl}_3}$

R—C(=O)—NH—CH₂—(Cl₂P—O) → R—C(=O)—NH—CH₂—(Cl₂P=O)

59

Ar₃C—OH $\xrightarrow{\text{PCl}_3}$ Ar₃C—O—PCl₃ $\xrightarrow{\text{−HCl}}$ Ar₃C—PCl₂

60

triarylcarbinols and PCl₃ to give triarylmethanephosphonic acids (**60**)[44a,99,100] can perhaps also be included.

Dialkyl phosphorochloridates (**61**) are known to react with 1-chloroethyl alkyl ethers to give the Arbuzov product **62**.[101] Silyloxymethyl derivatives of phos-

61 + **62** scheme

phonites (**63**) are also known to give Arbuzov product **64** on reaction with halides and hydrolysis, in 91% yield.[102]

Me₃SiOCH₂—P(OSiMe₃)(OSiMe₃) $\xrightarrow{\text{Cl—CH}_2\text{CH}_2\text{CN}}$ HO—P(=O)(CH₂OH)—CH₂CH₂CN

63   **64**
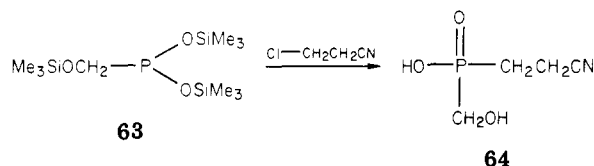
Of interest also is the reaction of the phosphonite **65** to give the Arbuzov product which cyclizes on reaction with the base to give 3-hydroxy-2-phospholene 1-oxide (**66**).[103]

R'—CH₂—P(OEt)(R) $\xrightarrow{\text{Br(CH}_2)_2\text{COOEt}}$ R'—CH₂—P⁺Br⁻[(CH₂)₂COOEt] $\xrightarrow[\text{(cyclization)}]{\text{base}}$ **66**

65

66

a, R = PhCH₂, OEt; R' = Ph
b, R = Et, OEt; R' = COOMe

C. Effectiveness of Catalysts

Normally the Arbuzov rearrangement proceeds without the help of catalysts, but in some situations catalysts are needed. For example, the reaction of iodobenzene with trialkyl phosphites does not proceed under normal conditions but may be photocatalyzed.[84,85,98] Certain metal halides also serve as catalysts. Thus the reaction of triethyl or triisopropyl phosphite with a number of unsaturated alkyl halides or aromatic halides is accelerated by nickel halides or copper powder. An even better catalyst is palladium chloride.[62,104–107] Other nickel and cobalt salts[108] such as Ni(CO)₄ and CoCl₂ have also been used. Very re-

cently hydroquinone,[108] phenothiazine,[94] and even acetic acid **65** have been used as catalysts.

An examination of a series of trialkyl phosphites showed[12] that heating them at 120 °C for 16 h did not bring about any isomerization. However on heating at 200 °C for 17.5 h the trimethyl phosphite underwent 100% conversion into dimethyl methanephosphonate, the ethyl ester remained stable, the isopropyl ester underwent 25% conversion into hydrogen phosphite and propylene, and the allyl ester polymerized.

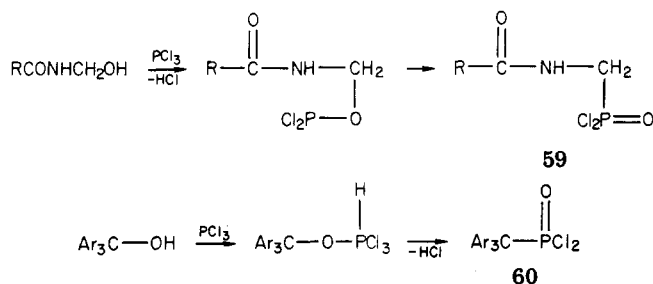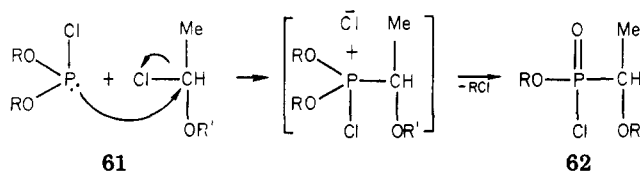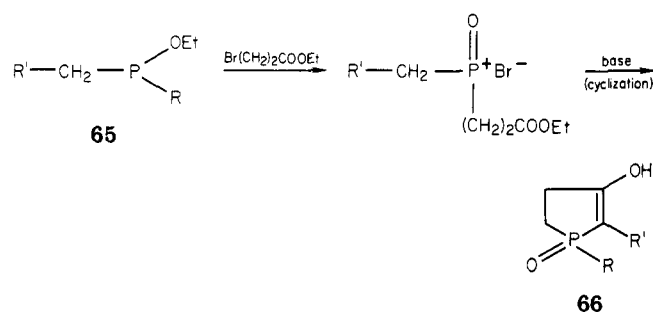Thus it could mean that a trialkyl phosphite by itself does not undergo the rearrangement to the phosphonate unless the necessary phosphorus compound or some other catalyst (like alkyl halides) is already present in the system in small amounts as an impurity.[109]

IV. Synthetic Applications

The Arbuzov reaction is the most widely used and versatile method for the formation of carbon–phosphorus bonds. Some of the most important classes of compounds prepared through this reaction are reviewed below.

A. Synthesis of Phosphonates

This is perhaps the most important class of compounds prepared by the Arbuzov rearrangement. The original observation that alkyl halides reacted with trialkyl phosphites to give the phosphonate esters **44** (see Scheme I) was found to hold good for a wide variety of substituents on both reactants. These have already been described in section III. Earlier work regarding the synthesis of phosphonates has been reviewed.[110]

Generally the reaction is carried out by heating the phosphite and alkyl halide to the required temperature until the reaction is complete. The reaction mixture is then usually subjected to fractional distillation. When the alkyl group of the phosphite and the halides are identical, only one phosphonate is formed. Where the alkyl halide employed is not identical with the one eliminated during the second stage of the reaction, a mixture may be formed. Even so the reaction can be controlled to give the desired product. In such cases it is decidedly advantageous to distil the alkyl halides generated during the reaction itself; for example, in the reaction of 1-chloromethylnaphthalene (**67**) with tri-

67 + (EtO)₃P (in small excess) $\xrightarrow[\text{−EtCl}]{150\text{–}60\,°C}$ 87%

67   **87%**
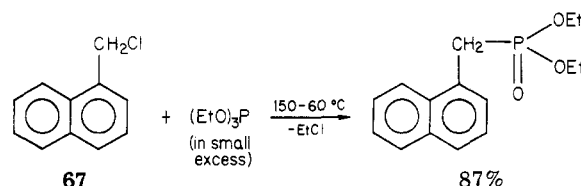
ethyl phosphite[111] the more volatile ethyl chloride formed during the reaction is continually distilled until the reaction is over.

When the alkyl halide employed and that formed during the reaction are of more or less the same reactivity, the control of reaction may be aided by the use of a large excess of the reactant. Thus when a mixture of 5 mol of trimethylene bromide and 1 mol of triethyl phosphite is refluxed under a fractionating column (for the removal of ethyl bromide as it is formed), the ester of bromopropionylphosphonic acid is obtained in 90% yield.[112]

In all these reactions, some complications might arise due to the self-alkylating ability of the trialkyl phosphites. Thus phosphonates are also formed during heating of trialkyl phosphites, especially in the presence of catalytic amounts of alcohol, alkyl halides, aluminum alkyls, inorganic iodides, or thermally from Cu(I) adducts.[43]

Solvents are, in general, not used, but sometimes they help better reaction control. An example is the internal Arbuzov rearrangement of 3 to 4, where the use of hydrocarbon solvents gives better results.[113]

B. Synthesis of Phosphinates

The dialkyl phosphonites also undergo Arbuzov rearrangement on treatment with alkyl halides, resulting in the formation of phosphinic acid derivatives 45 (see Scheme I). This is a major route for the synthesis of the esters of alkylaryl- and unsymmetrical dialkylphosphinic acid derivatives. The majority of the reactions which have been described involved unsubstituted saturated or unsaturated aliphatic or side-chain aromatic halides and unsubstituted phosphonites and therefore give products which contain only hydrocarbon groups. However, all the halides capable of undergoing S_N2 displacements may be used in this synthesis, and a variety of substituents may be used in the phosphonite too.

The reaction of a phosphonite with a dihalide may result in the formation of either esters of haloalkylphosphinic acids[114,115] or of diphosphinic acids.[116-118] The latter can also be prepared by the reaction of alkyl halides on diphosphinites.[119] Similarly the reaction of diphosphonites and dihalides yields polyphosphonites.[120] Likewise, ω-haloalkyl phosphonite esters yield cyclic phosphinates[121,122] (68) by intramolecular rearrangement; e.g.


68
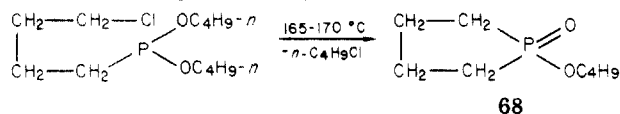
These reactions are typically carried out by mixing the phosphonite and the halide at room temperature, heating the reaction mixture slowly, controlling the reaction in case it tends to become vigorous, and finally maintaining the reaction at 120–160 °C for several hours. The yields are generally around 80%, but sometimes overheating causes some pyrolysis of the ester to acid,[123] and consequently lower yields.

In dialkyl phosphonites, the R directly attached to phosphorus is known to contain halogen-substituted aromatic,[124] dialkylamino,[125] and keto and ester groupings,[126] but in general the substituted phosphonites are not easily available. The R of the alkyl halide, the other reactant used in the reaction, could contain functional groups such as alkoxy,[127-129] alkylthio,[130] acyloxy,[128] carboxylic esters,[49,129,131] tertiary amides,[129,132,133] carbothiolic ester,[134] nitrite,[135] and tertiary amino groups.[129] However, groups such as hydroxy, thiol, carboxylic acid, and primary or secondary amines are not to be found for the simple reason that these substituents themselves reacts with phosphonites.

Due to their high reactivity, acyl halides react at much lower temperatures, yielding esters of acyl phosphinic acids.[136,137] Chloroacetone yields (61%) isopropenyl phosphonates (69)[138] whereas bromoacetone

gives 2-oxopropylphosphinates (70)[138,139] as the major product, with a minor quantity of 69.
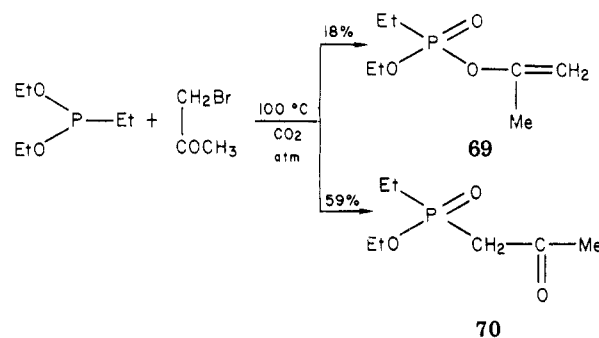
The acetals of α-haloacetaldehydes and those of β-halo aldehydes react normally to give the acetals or enol esters,[140,141] and these can be converted easily to aldehydoalkyl phosphinates. However, α-haloacetaldehydes themselves yield vinyl esters of phosphonates.

There are examples of some unusually substituted halides which, however, undergo the normal reaction, e.g., phthalimido group,[142] a variety of silicon-containing substituents,[143] sulfonyl fluorides,[144] sulfonate ester groups,[145] and butyl bis(chloromethyl)phosphinate (71), yielding the triphosphinate ester 72.[146]

71

72
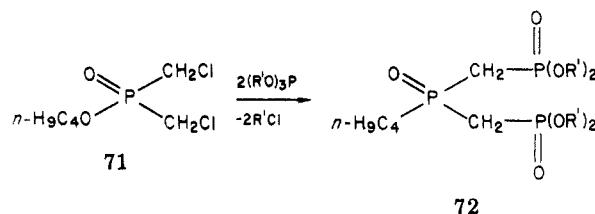
There are many examples of phosphonites with allyl- and benzyl-type halides, but examples involving secondary or tertiary halides of any kind are limited to reactions of isopropyl iodide,[48] dimethylphenyl chloride and bromide,[131,147] triphenylmethyl bromide,[148] and a few other substituted secondary or tertiary halides.[129,131,140,149] Even more limited are examples of vinyl halides: perfluoropropene[150,151] which reacts at the 1-position, 1-chloroperfluorocyclopentene which reacts with the replacement of the 2-fluoro atom,[152] 1-2-dichloroperfluorocyclopentene in which both chlorine atoms are replaced to give a diphosphinate,[153] and 1-cyanovinyl bromide[154] (α-bromoacrylonitrile), and benzenesulfenyl- and phenyl sulfonylvinyl bromides[155] which, whether 1- or trans-2-substituted, react to give trans-2-substituted products.

There is one instance of an Arbuzov-type reaction with a diaryl phosphonite[156] in which a quasi-phosphonium intermediate forms readily, but because it is very stable, an alkaline hydrolysis is necessary to obtain the aryl phosphinate. With carbon tetrachloride the phosphonites also react, apparently by a free-radical mechanism, as in the case of the reaction of phosphites with CCl_4,[81] either at room temperature,[157] during 20 min on a steam bath,[132] or on refluxing at 70–80 °C.[158,159]

Sometimes Arbuzov reactions proceed without addition of halides, but they are probably catalyzed by the impurities during the distillation of the phosphonites.[160,161] True uncatalyzed rearrangements of ordinary pure phosphonites occur at 240 °C or higher.[162] However, 2-chloroalkyl esters of phosphorus acids get isom-

erized to 2-chloroalkyl phosphinates (**73**) around 150 °C.[163-165]

$$Ar = C_6H_5, \ p\text{-}ClC_6H_4, \ p\text{-}MeOC_6H_4, \text{ etc.}$$
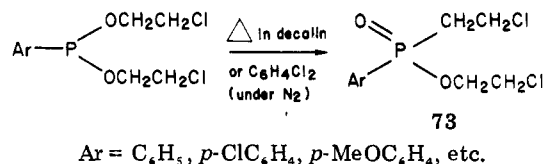
The conversion of the 1,3-dichloro-2-propyl phosphonite (**74**) into 2,3-dichloro-1-propyl phosphinate **76**[166] provides evidence for the formation of a quasiphosphonium intermediate **75**: **76** must have been formed through the intermediacy of **75**.
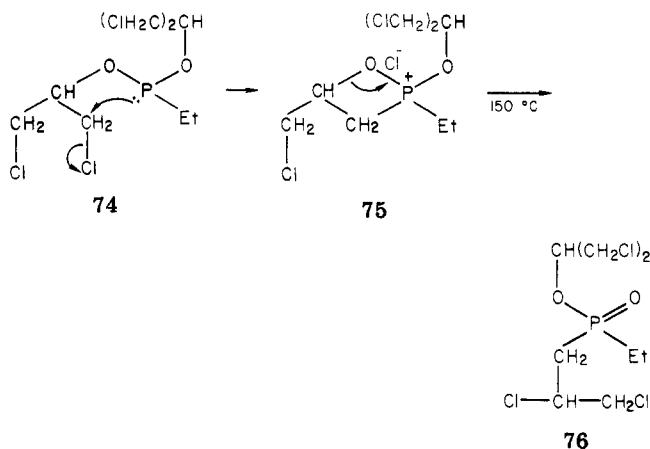
Allyl phosphonites are reported[158,167] to isomerize to allyl phosphinates during distillation or upon heating to 110–140 °C. During the thermal rearrangement of phosphonous and phosphinous allyl esters[168] there is interconversion of 1-methylallyl and but-2-enyl groups. Likewise crude alk-1-ynyl phosphonites rearrange at room temperature to give alka-1,2-dienyl phosphinates.[169-173] The above instances also point to the formation of cyclic transition states in these reactions.

C. Synthesis of Tertiary Phosphine Oxides

A convenient route to prepare tertiary phosphine oxides **46** consists in the reaction of phosphinite esters with alkyl halides (Scheme I). In general, the phosphinite esters undergo the Michaelis–Arbuzov reaction quite readily. Ethyl diethylphosphinite reacts with ethyl iodide at 45 °C and within 5 h. Methyl iodide reacts very vigorously even at room temperature to yield diethyl methyl phosphine oxide.[174] Aryl-substituted phosphinite esters such as methyl diphenylphosphinite appear to be less reactive than the alkyl analogues, since their reaction with methyl iodide could be controlled.[175]

A wide variety of alkylating agents have been used in the reaction: primary and secondary alkyl chlorides, bromide, and iodides, α-halo ketones, α-halo esters, α-acetyl chloride, benzal chloride, ethyl chloroformate, triphenylmethyl bromide and cycloalkylvinyl halides.[176]

It has been shown, by using differential thermal analysis, that the ease of rearrangement for various substituents[162,177] is 2-alkynyl > 2,3-alkadienyl > 2-alkenyl > alkyl.

The reaction in the latter case has been shown to be intermolecular and is catalyzed by alkyl halides.

Aryl halides do not seem to react with phosphinite esters. It is expected that, by analogy with other

phosphorus ester reactions,[4] this reaction would be difficult. The reluctance of aryl groups to undergo nucleophilic substitutions hinders the formation of phosphine oxides. Thus, it is reported[108] that phenyl diphenylphosphinite reacted with methyl iodide to give a solid (**77**) which was quite stable to heating.
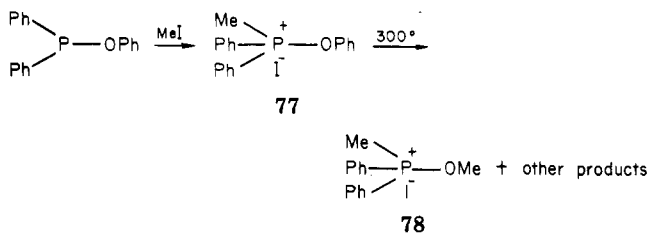
Pyrolysis of **77** resulted in the formation of **78**, iodobenzene, and an unidentifiable solid. Other phenoxyphosphonium salts have been transformed into phosphine oxides by treatment with water[178] and aqueous base[179] or by heating[179] (eq 8).
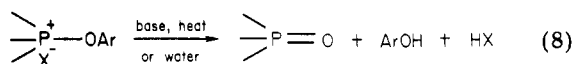
It is worth noting that the alkyl halides R'X which are frequently produced during the reaction are capable of alkylating the starting esters. In such cases a mixture of phosphine oxides is produced which makes the workup procedure complicated.

Some phosphinite esters undergo "self-isomerization" to the corresponding phosphine oxides; in other words they get isomerized even in absence of halides (eq 9).
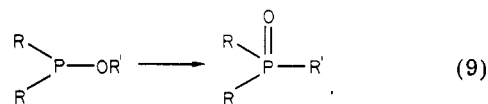
The isomerization may be effected by heating and is catalyzed by impurities present in the reaction mixture or by the addition of small quantities of iodine or alkyl halides.[175] In fact, it is quite often difficult to isolate the phosphinite ester because of the ease of its further isomerization. Thus earlier attempts[175] to prepare methyl and benzyl diphenylphosphinite failed as they resulted in the formation of phosphine oxides.

Some allyl phosphinites **79** are very reactive to thermal self-isomerization;[168,180-183] so are the 2-alkynyl phosphinites **80**.[32,169,184,185] On the basis of extensive experimental evidence, the mechanism of self-isomerization of these esters has been shown to involve concerted intramolecular processes (eq 10, 11). In this
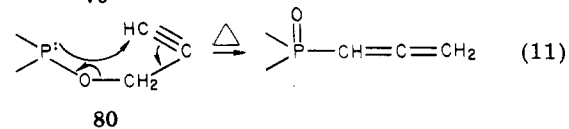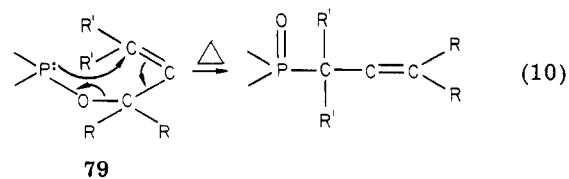
self-isomerization the classical phosphonium intermediates are probably not involved, and, therefore, they are somewhat different from the classical Michaelis–Arbuzov reaction.

The scarce availability of the starting phosphinite esters acts as a limiting factor in the synthesis of the phosphine oxides. It has been reported[186,187] that these esters could also be obtained as in eq 12 and 13, which increases the scope of this reaction.

$$3R_2N-P\begin{smallmatrix}Cl\\Cl\end{smallmatrix} + 2R'_3Al \xrightarrow[-2AlCl_3]{} 3R_2N-P\begin{smallmatrix}R'\\R'\end{smallmatrix} \quad (12)$$

$$R_2N-P\begin{smallmatrix}R'\\R'\end{smallmatrix} + R''-OH \xrightarrow[-R_2NH]{} R''O-P\begin{smallmatrix}R'\\R'\end{smallmatrix} \quad (13)$$
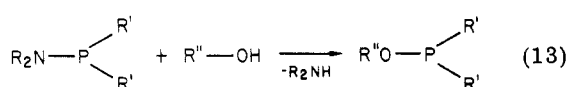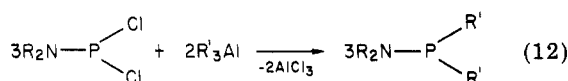
High overall yields of phosphine oxides are obtained when unsaturated alcohols, functionally substituted alcohols, and α,ω-alkanediols are employed (eq 14).

$$2\; \begin{smallmatrix}R'\\R'\end{smallmatrix}P-NR_2 \xrightarrow{HO(CH_2)_nOH} \cdots \xrightarrow{(CH_2)_n\begin{smallmatrix}Br\\Br\end{smallmatrix}} \cdots \begin{smallmatrix}R'\\R'\end{smallmatrix}\overset{O}{P}(CH_2)_n\overset{O}{P}\begin{smallmatrix}R'\\R'\end{smallmatrix} \quad (14)$$

81

Several novel compounds containing up to four phosphorus atoms have been prepared[187-193] in high yields by the use of the Michaelis–Arbuzov phosphinite reaction, for example, 82.

$$\begin{smallmatrix}R\\R\end{smallmatrix}P-OR' + (ClCH_2)_3P=O \longrightarrow \left(\begin{smallmatrix}R\\R\end{smallmatrix}\overset{O}{P}-CH_2\right)_3 P=O$$

82

D. Synthesis of Phosphonyl and Phosphinyl Halides

Besides the phosphites described earlier, certain trivalent phosphorus compounds of the type 83 also undergo the Michaelis–Arbuzov rearrangement.

$$R-Z-P\begin{smallmatrix}Cl\\Cl\end{smallmatrix} \longrightarrow R-\overset{Z}{P}\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$$

83   Z = O or S

Though catalysts are required,[194,195] the isomerization is also known to take place without them. Propargyl esters 84 for example, rearrange readily.[196-198]

$$R''-C\equiv C-O-P\begin{smallmatrix}Cl\\Cl\end{smallmatrix} \qquad \begin{smallmatrix}R\\R'\end{smallmatrix}C=C=\overset{O}{C}-\overset{O}{P}\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$$

84

N-Hydroxymethyl carboxylic amides yield normal alkyl phosphorodichloridates, $ROPCl_2$, on treatment with PCl_3. On prolonged standing the $ROPCl_2$ isomerizes to phosphonyl dichloride, warming with acetic anhydride favoring the reaction. Specific phosphonyl

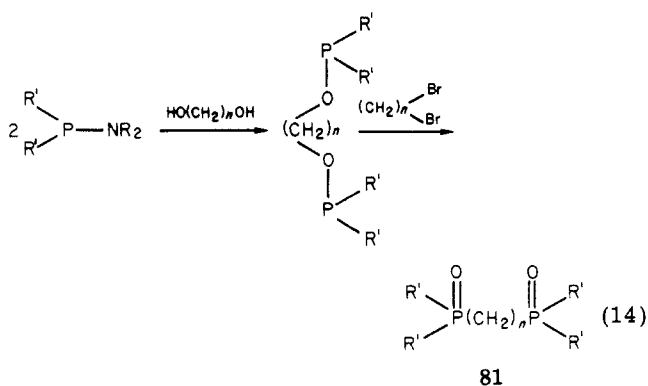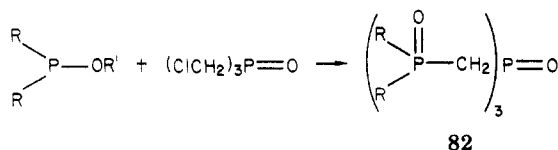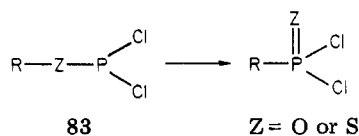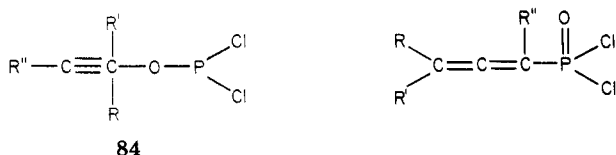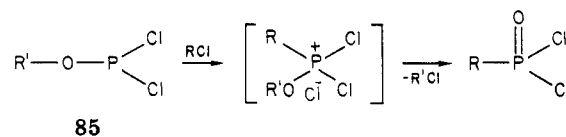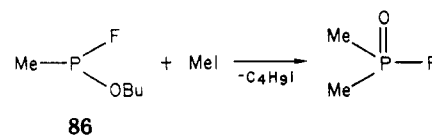dichlorides have not been isolated in the reactions as the products are directly hydrolyzed to the phosphonic acids. (Hydroxymethylene)camphor also reacts in an analogous manner.[199]

The alkyl phosphorodichloridates 85 react at elevated temperature in the presence of alkyl halides.[200-203]

$$R'-O-P\begin{smallmatrix}Cl\\Cl\end{smallmatrix} \xrightarrow{RCl} \left[\begin{smallmatrix}R\\R'O\end{smallmatrix}\overset{+}{\underset{Cl^-}{P}}\begin{smallmatrix}Cl\\Cl\end{smallmatrix}\right] \xrightarrow{-R'Cl} R-\overset{O}{P}\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$$

85

Nickel iodide or ferric chloride catalyzes the reaction.[201,202] Phosphonofluoridite esters (86)[204] also react similarly.

$$Me-P\begin{smallmatrix}F\\OBu\end{smallmatrix} + MeI \xrightarrow{-C_4H_9I} \begin{smallmatrix}Me\\Me\end{smallmatrix}\overset{O}{P}-F$$

86

In the presence of ferric chloride as catalyst, even functional alkyl halides 87 have been reported[205] to react with 85.

$$85 + ClCH_2NCO \xrightarrow{-R'Cl} ONC-CH_2-\overset{O}{P}\begin{smallmatrix}Cl\\Cl\end{smallmatrix} \quad (15)$$

87
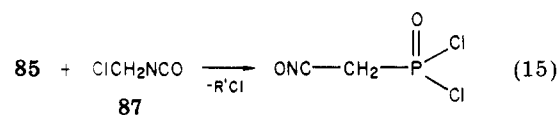
In a variation of the reaction, halogen has also been used[206] instead of alkyl halide (eq 16).

$$Me-P\begin{smallmatrix}F\\OR\end{smallmatrix} + Br_2 \longrightarrow Me-\overset{O}{P}\begin{smallmatrix}F\\Br\end{smallmatrix} + RBr \quad (16)$$
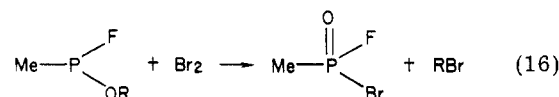
E. Other Synthetic Applications

The usefulness of the Michaelis–Arbuzov rearrangement in the synthesis of phosphonolipids which are more stable than phospholipids in the body fluid is attracting much attention in chemotherapeutic research. The procedure followed[207] is depicted in Scheme II.

The conversion of (2-phthalimidoethyl)phosphonic acid (88) into phosphonolipids is known in the literature.

Certain alkyl halides which are not otherwise readily accessible[16] can be made by the Michaelis–Arbuzov rearrangement. An example is neopentyl halide (eq 17).

$$\begin{smallmatrix}ArO\\ArO\\ArO\end{smallmatrix}P + R'-hal \longrightarrow \begin{smallmatrix}ArO\\ArO\end{smallmatrix}\overset{+}{\underset{hal^-}{P}}\begin{smallmatrix}OR\\R'\end{smallmatrix} \xrightarrow{ROH} \left[\begin{smallmatrix}ArO\\ArO\end{smallmatrix}\overset{+}{\underset{hal^-}{P}}\begin{smallmatrix}OR\\R\end{smallmatrix}\right] \longrightarrow$$

89

$$\begin{smallmatrix}ArO\\ArO\end{smallmatrix}\overset{O}{P}\begin{smallmatrix}\\R'\end{smallmatrix} + R-hal \quad (17)$$
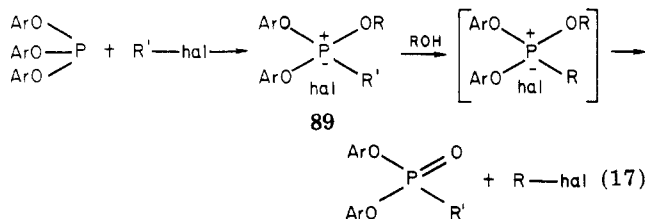
The phosphonium salt 89 is quite stable. If it is treated with an alcohol, an aryloxy group is replaced by an alkoxy group, followed by the rearrangement in the normal way.

The Arbuzov rearrangement has also been used as a new means of synthesis of sulfonophosphono ethylenes (90) and diphosphonoethylenes (91)[208] (Scheme III).

The rearrangement is also used in the preparation of the starting materials (phosphonates) needed in the

SCHEME II. Synthesis of Phosphonolipids

88

SCHEME III. Synthesis of Sulfonophosphono- and Diphosphonoethylenes

91, R = MeO, Ph, EtO
  R' = MeO, Ph, EtO
  R'' = MeO, Ph, EtO
  R''' = MeO, Ph, EtO

90, R = Ph, PhCH$_2$, Et, Me
  R' = MeO, EtO, Ph
  R' = MeO, EtO, Ph

Horners–Wadsworth modification of the Wittig reaction[209] and in the structure determination of triphosphites of D-mannitol and DL-xylitol.[210] The cyclic phosphites are heated with ethyl bromide under Arbuzov conditions, and on the basis of the structure of the phosphonate obtained, the configuration of phosphite of the hexose can be determined.

V. Behavior of Sulfur and Fluorine Analogues under Arbuzov Conditions

A. Trialkyl Trithiophosphites

Trialkyl trithiophosphites are reported[211] to react by a mutual exchange process which is in sharp contrast to the behavior of trialkyl phosphites. The mutual exchange process has been applied for the synthesis of thiophosphorochloridites (92) and dichloridites (93).
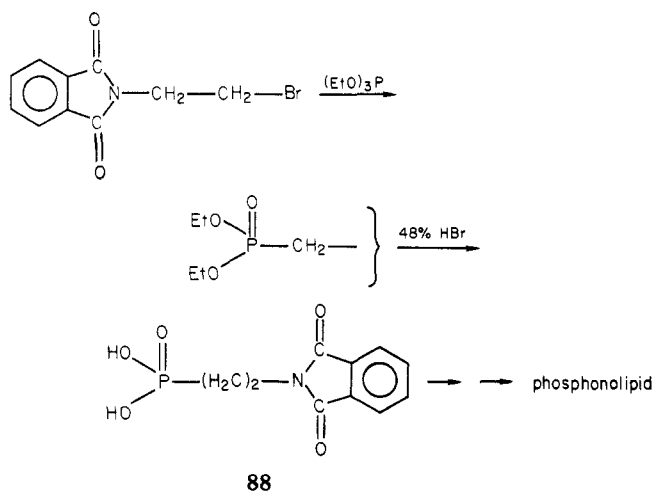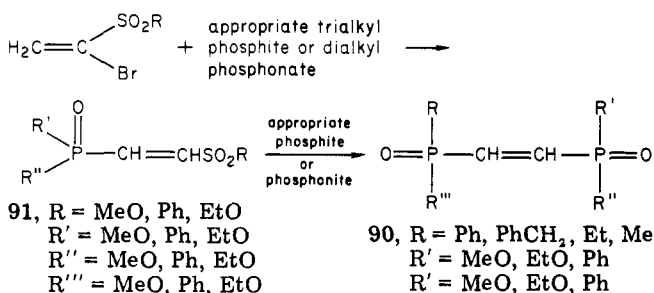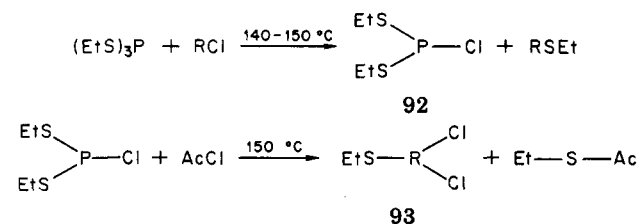

92

93

Triphenyl trithiophosphite also reacts similarly.[212] A explanation could be that as the sulfur atom has vacant d orbitals (unlike the oxygen which has none), it could enter into a partial double bond formation with the unshared pair of electron on phosphorus. Consequently the unshared electron pair is localized more toward sulfur, making it more nucleophilic than phosphorus. The electron-rich sulfur now attacks the alkyl halide

as a nucleophile, resulting in the cleavage of the sulfur–phosphorus bond to form 92 and 93.

B. Alkyl Phosphonodithioites

Dialkyl phosphonodithioites react with alkyl halides at 130–150 °C to give, by rearrangement, dialkyl phosphinodithioates (94) as the major product together

94
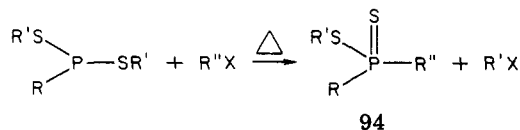
with a variety of other minor products. A number of phosphinodithioates have been prepared in this manner.[213-216]

C. Phosphinodithioites

Phosphinodithioites are also known to isomerize into phosphine sulfides (95) under Arbuzov conditions[175] (eq 18). The reaction has not been investigated in as much

95
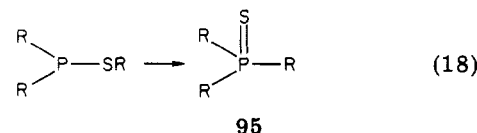
detail as that of the oxygen analogues—the phosphinites. The mechanism is believed to be similar (eq 19, 20).
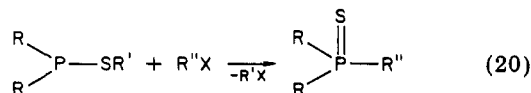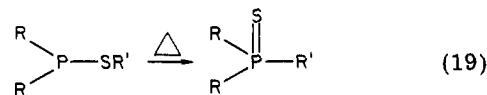
Perhaps due to the lesser strength of the carbon–sulfur bond as compared to the carbon–oxygen bond, the rearrangement of the sulfur analogues is more rapid than that of the phosphinites.[217,218] The intermediate phosphonium salts also can be isolated if the reaction is carried out at low temperature.[219]

In a similar manner alkyl phosphonamidothionites (96) also rearrange to phosphine sulfides on reaction with alkyl halides.[220]

96
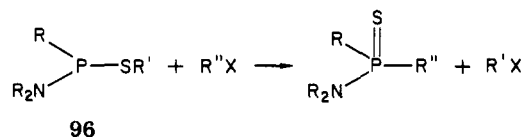
D. Organofluorine Compounds

Under Michaelis–Arbuzov conditions alkyl fluorides and phosphites react to give abnormal products[221] (eq 21).
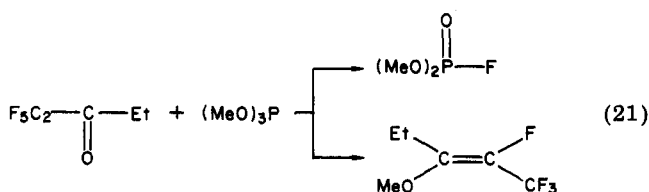
SCHEME IV. Abnormal Reaction of Fluoro Compounds with Trialkyl Phosphites

97

(not formed)
a, R = Me, Et; R' = Me
b, R = Et, Me; R' = Et
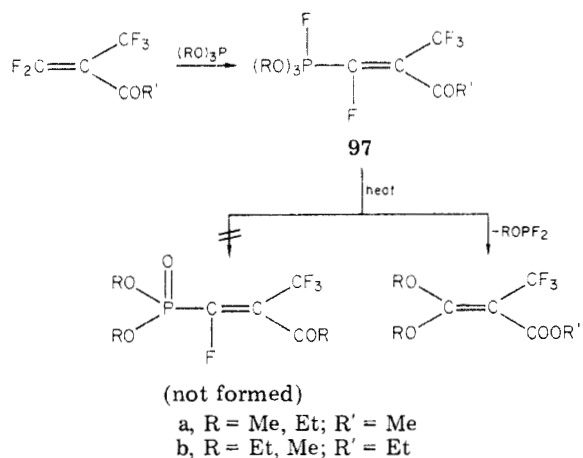
Fluorinated ketones also react unusually with silyl and acetyl phosphites[222] (eq 22, 23).
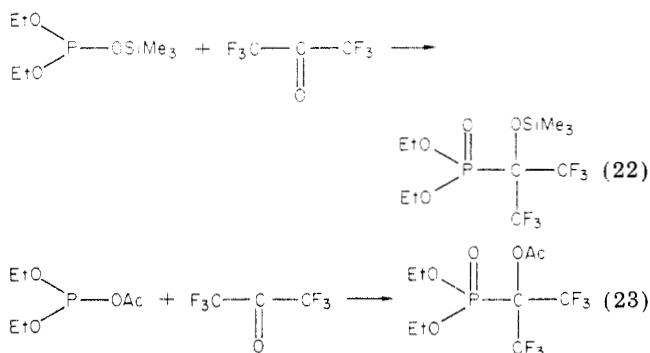
Perfluoromethacrylic acid forms an adduct (**97**) with trialkyl phosphites which splits in an abnormal way[223] (Scheme IV).

Very recently polyfluoroaromatic compounds containing activated fluorine atoms have been reported to react in the Arbuzov way with trialkyl phosphites.[224]

VI. Rearrangement of Phosphites in the Presence of Compounds Not Containing Halogen

Generally the presence of alkyl halides is essential for the rearrangement as they enter into a reaction with phosphite forming the phosphonium intermediate which then splits in the Arbuzov manner. However, rearrangement is also known to occur in the presence of reactants which contain no halogen. Thus dialkyl sulfates,[16] alkyl p-toluenesulfonates,[225] alkyl fluoroborates, and lactones also react with trialkyl phosphites in the usual manner to give **98**.[226,227]

98
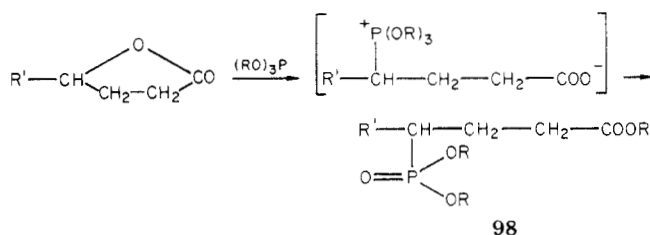
Other alkylating and acylating agents which react according to an Arbuzov scheme are lactams,[226,228] sulfones,[229] salts of Mannich bases,[230] and carboxylic acid anhydride.[231]

Nitro groups are usually reduced by tervalent phosphorus esters, but o-dinitrobenzene is known to react with diethyl methylphosphonite to give an o-nitrophenyl phosphinate (**99**).[232] Nitro olefins are also reported[233] to react similarly with trialkyl phosphites in an Arbuzov manner, yielding **100**.

99

100

R = Me, Et, Pr, Bu; R' = H, Me
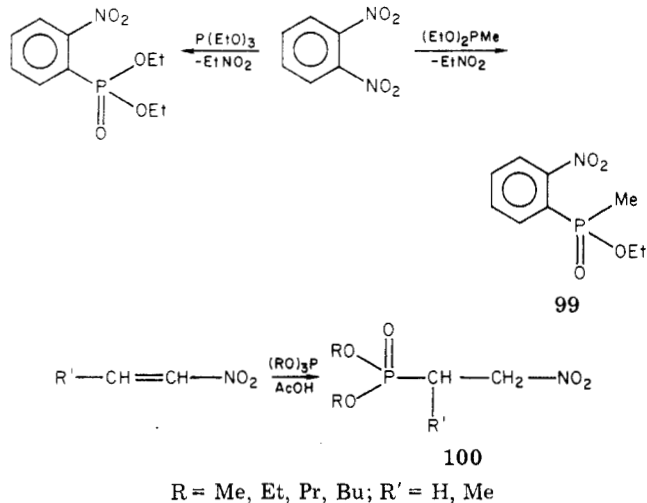
Hydroxymethyl amides are also known to react with phosphites in the usual manner, e.g., 3-bromo-N-(hydroxymethyl)benzamide (**101**) reacts with trimethyl phosphite to give the phosphonate.[234]

101
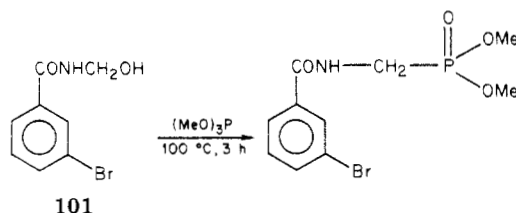
Free radicals are known to bring about the rearrangement of phosphinite esters to phosphine oxides. Thus, dimethylamine radicals initiated the chain reaction for the conversion of methyl diphenylphosphinite (**102**) into methyldiphenylphosphine oxide[235] and of

102   (initiation)
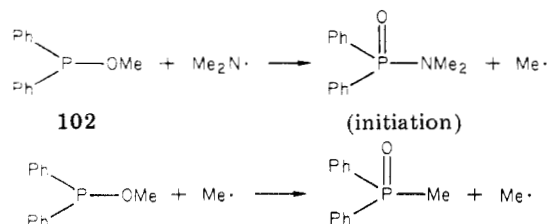
cyclic phosphites into phosphonates.[27c]

Methyl and isopropyl radicals generated by the photolysis of azoalkanes reacted with **102** to yield methyl-(33%) and isopropyldiphenylphosphine oxide (80%).[236] Benzyl radicals were found unreactive whereas *tert*-butyl radicals[236] merely initiated the rearrangement reaction. Phenyl radicals gave triphenylphosphine oxides in moderate yield when reacted with various alkyl diphenylphosphinates.[236]

Tricarbonylcyclohexadienyliron tetrafluoroborate (**103**) has been recently reported[237] to react with trimethyl phosphite to give the Arbuzov product **104**. Reaction with FeCl₃ is known to remove the tricarbonyl iron group from **104**.

103 reacted with aqueous hypophosphorus acid (2 h, 65 °C) to give the phosphinic acid **105**, converted to **106**

103

104
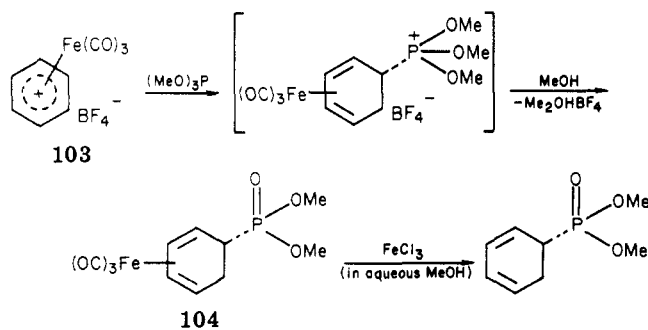
by mercuric oxide in benzene.

105

106
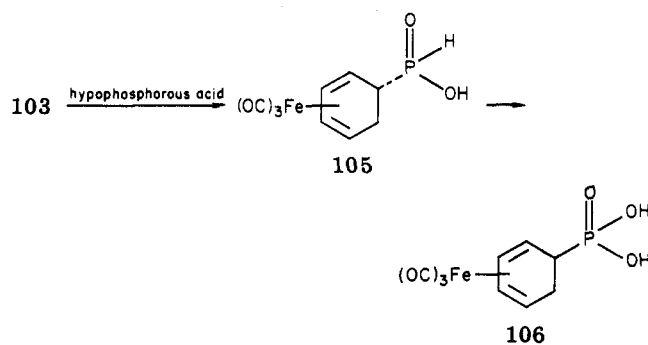
Similarly the unsubstituted **107** derived from $(-)$-α-phellandrene gave the corresponding dimethyl phosphonate **108** when reacted with trimethyl phosphite.[237]

107   **108**
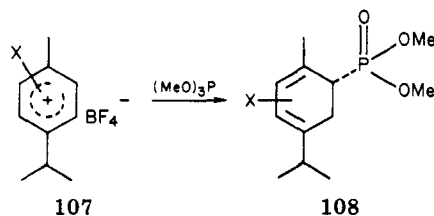
A very interesting variation of the Arbuzov rearrangement is reported by Bogatskii and co-workers[238] who observed that the cyclic phosphite **109** undergoes rearrangement to **110** on treatment with methanol in the presence of AB-17-P anionic ion-exchange resin in the HO from, at atmospheric pressure and -5 °C temperature.   **110** had been reported previously as ob-

109, R = Cl   **110**
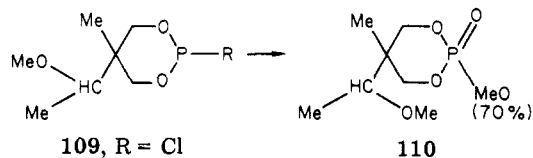
tainable from **109** by successive reaction with methanol and methyl iodide under pressure and elevated temperatures. Analogues of **109** reacted similarly, and the mechanism of formation of **110** under such conditions appears to be a new form of Arbuzov reaction. The intermediate methyl phosphite ester (**109**, R = OMe) underwent conversion to **110** by contact with anionic resin at -5 °C.

The same authors have recently reported[239] a similar variation of the Arbuzov rearrangement in 2-chlorodioxaphosphorinanes (**111**).

111 underwent rearrangement in methanol in the presence of anionic AB-17 resin to give the cyclic phosphonate **112**. **111** (R = OMe) was not an intermediate in the AB-17-induced rearrangement.

111   **112**
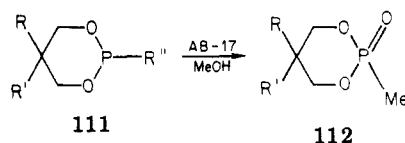
R = R′ = alkyl, alkoxyalkyl; R″ = Cl

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