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The Arbuzov Rearrangement with Participation of Halogenoacetylenes as a Method of Synthesis of Ethynylphosphonates and other Organophosphorus Compounds

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The Arbuzov rearrangement with participation of halogenoacetylenes is examined and its possible application in the synthesis of a wide variety of hitherto inaccessible organophosphorus compounds is discussed.
The bibliography includes 50 references.

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I. INTRODUCTION

The Arbuzov rearrangement, discovered at the beginning of the century, has served for decades as one of the principal methods of synthesis of compounds with a phosphorus–carbon bond and has been an important method for the investigation of substances capable of nucleophilic substitution and addition reactions. Studies carried out in the Department of Organic Chemistry of the Lensovet Leningrad Technological Institute showed in 1962 that halogenoacetylenes with the halogen attached to the triple bond can be used successfully in this reaction[1]. The discovery of the Arbuzov rearrangement involving halogenoacetylenes not only revealed a new pathway to the synthesis of a wide variety of acetylenic phosphonates and other organophosphorus compounds based on them but also attracted attention to the study of the reactivities of halogenoacetylenes in relation to nucleophiles.

Although many halogenoacetylenes have long been known and convenient preparative methods for the synthesis of a series of compounds of this type have been proposed, for a long time they did not find applications in organic synthesis. At the beginning of the 1960s only a few reactions involving the nucleophilic substitution of the halogen in halogenoacetylenes were known[2] and on the whole it was assumed that their reactivity in relation to nucleophiles is low. It was postulated that, as in hypohalites, the halogen in halogenoacetylenes is "positive" and that this should promote oxidation-reduction processes and not nucleophilic substitution with elimination of the halogen as an anion. In reality, it was found that, at least in those cases where the second carbon of the halogenoacetylenes is linked to a group containing a multiple bond, to an aromatic ring, or to a heteroatom, the nucleophilic substitution of the halogen—the Arbuzov rearrangement leading to the formation of "normal" products (ethynylphosphonates and halogenoalkanes)—takes place readily and with a high yield[3-7]:

$$R{-}C{\equiv}C{-}X + P(OAlk)_3 \longrightarrow R{-}C{\equiv}C{-}P(O)(OAlk)_2 + AlkX \quad (X=Cl, Br)$$

During the past two decades, various investigators achieved the syntheses of a wide variety of ethynylphosphonates, including those hitherto inaccessible, studied the reaction mechanism, and demonstrated the possibility of employing the compounds obtained for the synthesis of various organophosphorus products based on them.

II. SYNTHESIS OF ACETYLENIC PHOSPHONATES

Among halogenoacetylenic compounds, bromoethynyl- and chloroethynyl-benzenes[1,2], conjugated bromoalkenynes[3,6], and bromoalkadiynes (1-bromopenta-1,3-diyne and 1-bromohexa-1,3-diyne)[4] were made to undergo the reaction successfully. Alkylhalogenoacetylenes are much less reactive and react only on heating, forming mixtures of products which are difficult to separate[5]. Nevertheless, when 1-bromo-oct-1-yne reacts with triethyl phosphite, the corresponding phosphonate is formed in a yield up to 20%; however, the authors showed that the reaction of 1-bromoalkynes with sodium dialkyl phosphites, which takes place at a reduced temperature (−70 °C) in tetrahydrofuran with a yield up to 75%,[7] constitutes a more suitable method of synthesis of alkylethynylphosphonates.

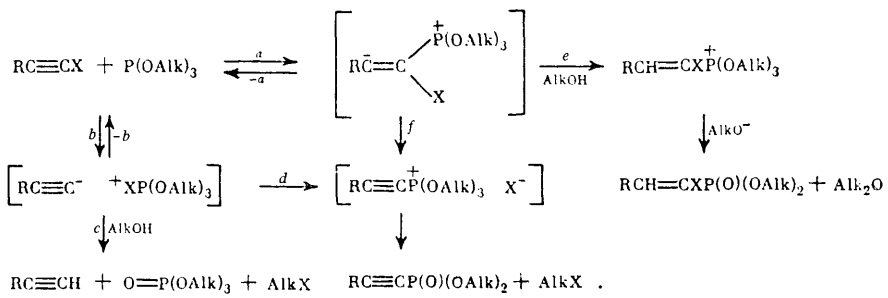
The rearrangement of trialkyl phosphites by halogenoacetylenes, containing a group with a metal belonging to the Fourth Period as the second substituent, has been achieved successfully. This not only permitted the synthesis of exotic dihetero-substituted acetylenes but also led to the discovery of a simple method of synthesis of unsubstituted ethynylphosphonate, which is otherwise difficult to obtain, and also of bromoethynyl phosphonate[9,10]:

$$Alk_3M{-}C{\equiv}C{-}X + P(OAlk)_3 \rightarrow Alk_3M{-}C{\equiv}C{-}P(O)(OAlk)_2 \rightarrow \begin{cases} \xrightarrow{\text{hydrolysis}} HC{\equiv}CP(O)(OAlk)_2 \\ \xrightarrow[(M=Sn)]{Br_2} BrC{\equiv}CP(O)(OAlk)_2 \end{cases} ; \quad M=Sn, Si$$

The rearrangement involving dichloro- and dibromo-acetylenes is especially interesting. Depending on the ratio of the dihalogenoacetylene and the phosphite, one or both halogen atoms can be substituted[5,11,12]:

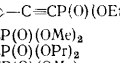
$$X{-}C{\equiv}C{-}X \xrightarrow{P(OAlk)_3} X{-}C{\equiv}C{-}P(O)(OAlk)_2 \rightarrow \xrightarrow{P(OAlk)_3} (AlkO)_2P(O)C{\equiv}CP(O)(OAlk)_2 .$$

This reaction has been used to synthesise symmetrical and mixed phosphonates[13]. The employment of this method for the synthesis of ethynylphosphine dioxides, which are of interest as dienophiles, has been reported[14]. In the presence of an excess of dihalogenoacetylene, highly reactive halogenoethynylphosphonates were obtained—they are convenient intermediates in the synthesis of previously inaccessible substituted ethynylphosphonates and derivatives of phosphonoacetic acid.



Ethynylphosphonates obtained by the Arbuzov rearrangement with participation of halogenoacetylenes, which were not indicated in a previous review[8], are listed in Table 1.

Table 1. Ethynylphosphonates obtained by the Arbuzov rearrangement from halogenoacetylenes*.

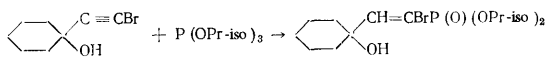
Compound	Yield, %	B.p., °C (*p*, mmHg)	*t*, °C	n_D^t, °C	d_4^t
$C_6H_{13}C{\equiv}CP(O)(OEt)_2$	15—20	128 (0.4)	20	1.4470	—
$CH_2{=}C(Et)C{\equiv}CP(O)(OMe)_2$	53	82 (0.15)	24	1.4818	1.127
$CH_2{=}C(Et)C{\equiv}CP(O)(OEt)_2$	60	82 (0.1)	25	1.4702	1.042
cis- $MeCH{=}C(Me)C{\equiv}CP(O)(OMe)_2$	52	90—95 (0.2)	23	1.5093	1.196
trans- $MeCH{=}C(Me)C{\equiv}CP(O)(OMe)_2$	30	81 (0.1)	24	1.4855	1.100
cis- $MeCH{=}C(Me)C{\equiv}CP(O)(OEt)_2$	52	102 (0.2)	20	1.4810	1.069
trans- $MeCH{=}C(Me)C{\equiv}CP(O)(OEt)_2$	57	86 (0.1)	23	1.4753	1.043
	77	147 (0.05)	23	1.5030	1.106
$ClC{\equiv}CP(O)(OMe)_2$	87	55 (2)	25	1.4569	—
$ClC{\equiv}CP(O)(OPr)_2$	84	98—99 (1)	20	1.4566	1.0978
$BrC{\equiv}CP(O)(OMe)_2$	62	89—91 (1)	20	1.4711	1.6308
$Me_3SiC{\equiv}CP(O)(OMe)_2$	70	60 (0.8)	20	1.4305	—
$Me_3SiC{\equiv}CP(O)(OEt)_2$	82	60—61 (0.01)	25	1.4437	—
$Et_3SnC{\equiv}CP(O)(OEt)_2$	82	150—151 (1)	20	1.4899	1.2797
$(MeO)_2P(O)C{\equiv}CP(O)(OMe)_2$	72	155—156 (1.5)	20	1.4473	—

Remarks. The table does not include compounds listed in the review of Ionin et al.[8] and a number of compounds quoted without an indication of the constants. A patent has been taken out[49] for a method of synthesis of the previously unknown[8] tetraethyl acetylenediphosphonate.

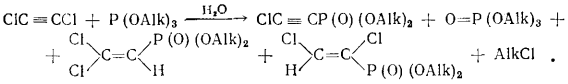
1. The Mechanism of the Rearrangement

Since the interaction of halogenoacetylenes with trialkyl phosphites is analogous to the usual rearrangement with participation of halogenoalkanes as regards the character of the rearrangement and the structure of the products, in this instance too one can put forward the usual mechanism of the rearrangement with the intermediate formation of a quasi-phosphonium compound[3]. Subsequent kinetic studies[15] confirmed the two-stage character of the rearrangement. The reaction is of second order (of first order with respect to each reactant). $\Delta H^{\neq} = 17-18$ kcal mol^{-1}, $-\Delta S^{\neq} = 26-29$ e.u. and the Hammett reaction constant $\rho \cong 2$ have been obtained for a series of chloro- and bromo-ethynylarenes p-$XC_6H_4C{\equiv}CY$ (X, Y = Cl, Cl; Cl, Br; H, Br; Me, Cl; Me, Br; MeO, Cl). The high negative activation entropy indicates the formation of a pair of ions in the rate-determining stage, which corresponds to a quasi-phosphonium mechanism of the rearrangement; the high value of ρ is an indication of the proximity of the reaction centre to the aryl group, which may correspond to attack by the nucleophile on the carbon atom nearest to the halogen (direction *a* in the scheme presented below). However, studies using a proton donor as a trap for the intermediate carbanions made it possible to specify the first stage in greater detail and to discover two possible directions of attack by the nucleophile—on the C(1) carbon atom and on the halogen atom X.[12,15,16]

Direction *b* has been confirmed by the formation of free acetylene (reduction, reaction *c*). Since the kinetic characteristics of the processes occurring when the reaction is carried out in the presence of alcohol change only slightly, the addition of a proton donor does not alter the mechanism radically. The occurrence of the reaction via pathway *e* has been confirmed experimentally in the interaction of tri-iso-propyl phosphite with 1-bromoethynylcyclohexanol[16]:



and the study of the interaction of dichloroacetylene with trialkyl phosphites, which in the presence of moisture takes place partly with formation of dihalogenovinylphosphonate[12,17]:



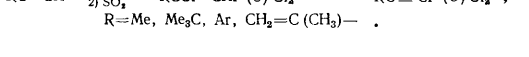
Thus the rearrangement proceeds via two competing pathways—with attack by the nucleophile on the C(1) atom and on the halogen atom.

The reactions of halogenoacetylenes with tertiary phosphines take place analogously but stop at the stage of the quaternary phosphonium salt[18—21].

2. Other Methods of Synthesis of Acetylenic Compounds With a Phosphorus-Containing Group At the Triple Bond

In order to assess the significance of the Arbuzov rearrangement as a method of synthesis of phosphonoacetylenic compounds, we shall consider other methods of synthesis of these substances[22,23]. The traditional method of synthesis of hetero-substituted acetylenes, namely the reaction involving metal acetylides, has been used mainly for the synthesis of compounds with a tricoordinate phosphorus atom and also for the preparation of unsubstituted ethynylphosphonate, which is difficult to obtain[8]. In the synthesis of higher derivatives, this method is relatively unsuitable owing to the difficulty of isolating the products.

The addition of phosphorus pentachloride to acetylenic hydrocarbons with subsequent dehydrochlorination is convenient for the synthesis of ethynylphosphonates but is restricted to a narrow range of compounds[24—26]:



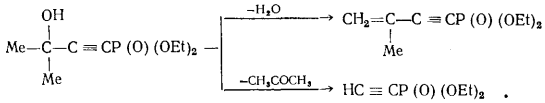
This method is inapplicable to higher alkylacetylenes, since it leads to phosphonates with multiple bonds remote from the phosphorus atom.

Phosphorus-containing propadiene derivatives readily undergo prototropic isomerisation with migration of the double bond to the phosphorus-containing group[27,28]. This property can be used for the synthesis of 1-propynylphosphonates and the analogous phosphine oxides in a single stage via the acetylene–allene–acetylene isomerisation of propargyl phosphites or propargyl phosphinites[29]:

$$(AlkO)_2POCH_2C\equiv CH \rightarrow CH_2=C=CHP(O)(OAlk)_2 \rightarrow MeC\equiv CP(O)(OAlk)_2 .$$

The reaction involving higher acetylenic phosphonates stops at the allene stage and prototropic isomerisation under the influence of bases leads to a mixture of compounds in which isomers with a triple bond remote from the phosphorus atom predominate[28].

The formation of certain acetylenic phosphonates by the reaction of halogenoacetylenes with sodium dialkyl phosphites was mentioned above. The phosphonoacetylenic alcohols obtained by this method were converted into other derivatives—halides, enynylphosphonates, and unsubstituted ethynylphosphonate[6]:



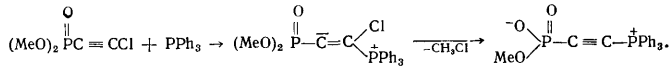
The formation of acetylenic phosphines by the reaction of phosphides with halogenoacetylenes is known[30]. The synthesis of a series of compounds with a phosphorus(III) atom at the triple bond has been reported: primary and tertiary phosphines, phosphinite esters, and *N,N*-dialkylphosphinamidates[31–33].

A number of acetylenic phosphonates have been obtained as a result of subsequent reactions of halogenoethynylphosphonates formed when dihalogenoacetylenes and trialkyl phosphites react. These reactions will be considered in the next section.

III. REACTIONS OF HALOGENOETHYNYLPHOSPHONATES

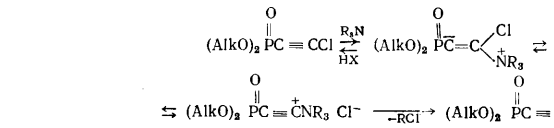
1. Reactions with Retention of the Triple Bond

Chloro- and bromo-ethynylphosphonates, obtained by the reaction of dihalogenoacetylenes with tertiary phosphites, contain a halogen atom at the triple bond activated by the electron-accepting dialkyl phosphonate group. These compounds are capable of nucleophilic substitution of the halogen with retention of the triple bond, which makes it possible to synthesise a wide variety of ethynylphosphonic acid derivatives hitherto inaccessible. The possibility of involving these compounds in the Arbuzov rearrangement with formation of ethylidynediphosphonates was mentioned above. The interaction of chloroethynylphosphonate with triphenylphosphine leads to the formation of a quaternary phosphonium salt, but the resulting chloride anion attacks another electrophilic centre (the phosphonate group), which leads to the formation of a dipolar ion[19]:



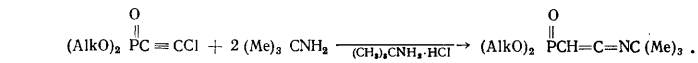
Chloroethynylphosphonates react vigorously with tertiary aliphatic amines forming ynammonium salts. In the case of triethylamine such a salt is unstable and decomposes with formation of an ynamine on slight heating[34].

The ynammonium salt obtained from trimethylamine is more stable and the formation of the ynamine requires heating to 150–160 °C. On treatment with proton donors, the salt decomposes with liberation of the initial chloroethynylphosphonate[17,35]:



Ynamines are formed readily also on interaction of chloroethynylphosphonates with secondary amines, but in this case a second mole of the amine combines with the hydrogen chloride evolved[35].

The reaction with a sterically hindered primary amine (t-butylamine) proceeds analogously, but the proton migrates in the product with formation of a keten imine structure[36]:



The reaction with ammonia involves the prototropic shift of two hydrogen atoms and the triple bond migrates to the nitrogen atom with formation of phosphonoacetonitrile[5].

Stronger nucleophiles (alkoxide anions) attack the chloroethynylphosphonate at the phosphono-group, which leads to the rupture of the P–C bond and the formation of phosphates. However, on treatment with the phenoxide anion, it is possible to achieve the substitution of the halogen with formation of phenoxyethynylphosphonates[17]:

$$(AlkO)_2P(O)C\equiv CCl \xrightarrow{PhO^-} (AlkO)_2P(O)C\equiv COPh + Cl^- .$$

Treatment of chloroethynylphosphonate with an equivalent amount of sodium ethanethiolate leads to the substitution of the halogen by the ethylthio-group[17]:

$$(AlkO)_2P(O)C\equiv CCl + EtS^- \rightarrow (AlkO)_2P(O)C\equiv CSEt + Cl^- .$$

Neither reaction goes to completion and in the presence of an excess of the nucleophile they are accompanied by the addition of the latter with formation of ethylenic compounds and phosphonoacetic acid derivatives.

Chloroethynylphosphonate is reactive toward organomagnesium compounds, which makes it possible to obtain alkylethynylphosphonates[5]:

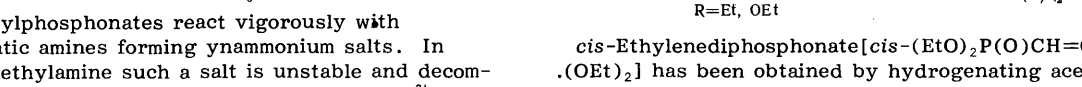
$$(AlkO)_2P(O)C\equiv CCl + EtMgBr \rightarrow (AlkO)_2P(O)C\equiv CEt .$$

The constants of the new compounds with a phosphorus-containing group at the triple bond are listed in Table 2.

2. Reactions Involving the Triple Bond

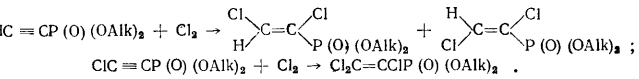
Ethynylphosphonates contain the highly reactive triple bond, which permits their use in the synthesis of a wide variety of organophosphorus compounds.

Catalytic hydrogenation of ethynylphosphonates at a palladium catalyst is stereospecific and *cis*-1-alkenylphosphonates are formed following the addition of one mole of hydrogen[25,37]:



cis-Ethylenediphosphonate[*cis*-$(EtO)_2P(O)CH=CHP(O).(OEt)_2$] has been obtained by hydrogenating acetylenediphosphonate.

Chlorination of ethynylphosphonate leads to the formation of a mixture of *cis*- and *trans*-addition products. The third (geminal) dichlorovinylphosphonate is formed in the Arbuzov rearrangement of dichloroacetylene and trialkyl phosphites in the presence of moisture (see Section II). Chlorination of chloroethynylphosphonate leads to the formation of a trichloroethylene derivative[12]:



Bromination results in a mixture of isomeric 1,2-dibromo-2-chlorovinylphosphonates[17].

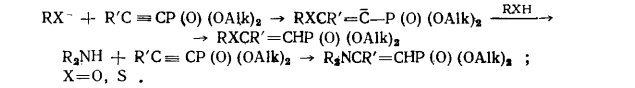
Table 2. Ethynylphosphonates obtained by different methods (other than the Arbuzov rearrangement)*.

Compound	Yield, %	B.p., °C (*p*, mmHg)	n_D^{20}	d_4^{20}
By the interaction of halogenoacetylenes with sodium dialkyl phosphites (Ref.7)				
MeC≡CP(O)(OEt)$_2$	37	84—87 (0.3)	1.4450	
EtC≡CP(O)(OEt)$_2$	40	100 (0.4)	1.4437 (23°)	
PrC≡CP(O)(OEt)$_2$	75	110 (0.4)	1.4463 (22°)	
BuC≡CP(O)(OEt)$_2$	70	115 (0.6)	1.4478 (24°)	
BuC≡CP(O)(OBu)$_2$	72	143 (0.5)	1.4503 (19°)	
AmC≡CP(O)(OEt)$_2$	72	125 (0.4)	1.4481 (22°)	
HexC≡CP(O)(OEt)$_2$	69	128 (0.4)	1.4470 (22°)	
HOCH$_2$C≡CP(O)(OEt)$_2$	18	160 (0.3)	1.4570	
HOCH(Me)C≡CP(O)(OEt)$_2$	60	162 (0.4)	1.4556 (21°)	
HOC(Me$_2$)C≡CP(O)(OEt)$_2$	68	133 (0.4)	1.4500 (25°)	
From carbinols, by the substitution of the hydroxy-group by halogen and dehydration (Ref.7)				
CH$_2$=C(Me)C≡CP(O)(OEt)$_2$	65	107 (0.5)	1.4630 (24°)	
CH$_2$CHClC≡CP(O)(OEt)$_2$	55	123 (1)	1.4586	
From 2-chloroalka-1,3-dienylphosphonates, by dehydrochlorination (Ref.26)				
CH$_2$=C(Me)C=CP(O)Cl$_2$	95	41—42 (0.05)	1.5165	1.2885
Me$_2$C=C(Me)C≡CP(O)Cl$_2$	67	70—71 (0.1)	1.5279	1.2210
MeCH=C(Me)C≡CP(O)Cl$_2$	70	47—48 (0.05)	1.5189	1.2379
By the substitution of chlorine in chloroethynylphosphonates (see Section III. 1)				
EtSC≡CP(O)(OEt)$_2$	48	132 (1)	1.1750	1.4909
Me$_2$NC≡CP(O)(OMe)$_2$	87	124 (1)	1.1970	1.4789
Me$_2$NC≡CP(O)(OEt)$_2$	84	129 (1)	1.1166	1.4741
Me$_2$NC≡CP(O)(OPr)$_2$	82	153 (1)	1.0385	1.4729
Et$_2$NC≡CP(O)(OMe)$_2$	84	131 (1)	1.1780	1.4763
Et$_2$NC≡CP(O)(OEt)$_2$	44	145—147 (1)	1.4680	1.0538
Et$_2$NC≡CP(O)(OPr)$_2$	79	168 (1)	1.4689	1.0245

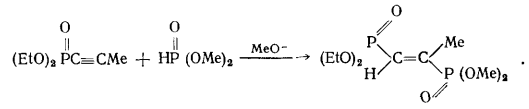
Note. The table does not include compounds quoted without an indication of their physicochemical constants.

The addition of hydrogen halides to phosphine oxide with a triple bond takes place with difficulty, which can be explained by the protonation of the phosphoryl oxygen. On the other hand, hydrochlorination of chloroethynylphosphonate takes place fairly readily and leads to the formation of a geminal dichloride[12,17].

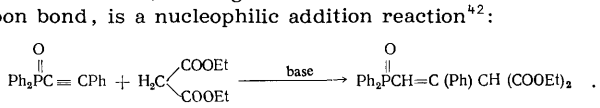
Ethynylphosphonates show a particular tendency to undergo nucleophilic addition reactions involving the triple bond. Alkoxide and thiolate anions as well as secondary amines attack the triple bond at the C(2) atom with formation of the corresponding 2-hetero-substituted vinylphosphonates[38-40]:



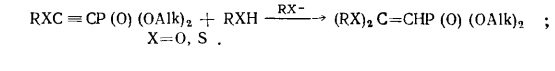
Dimethyl phosphite adds to the 1-propynylphosphonic ester with formation of the *E*-isomer of 1,2-propylenediphosphonate[41]:



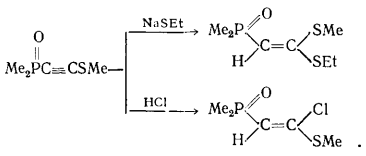
The condensation of diphenyl(phenylethynyl) phosphine with malonic ester, leading to the formation of a new carbon–carbon bond, is a nucleophilic addition reaction[42]:



Alkoxy- and alkylthio-ethynylphosphonates combine with a nucleophile at the C(2) atom with formation of 2,2-dihetero-substituted vinylphosphonates[17]:

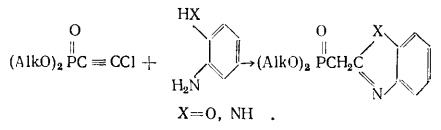


It has been shown[43] that the addition of a mercaptan and hydrogen chloride to dimethyl(methylthioethynyl)phosphine oxide proceeds in the same manner:

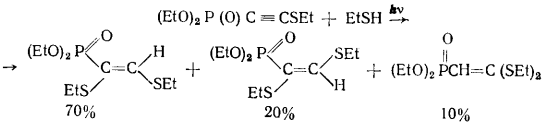


Hydration of hetero-substituted ethynylphosphonates results in the formation of phosphonoacetic acid derivatives.

Treatment of halogenoethynylphosphonates with an excess of a nucleophile results in the substitution of the halogen and the addition of the nucleophile to the triple bond. Bifunctional nucleophiles lead to the formation of heterocyclic compounds[44,45]:

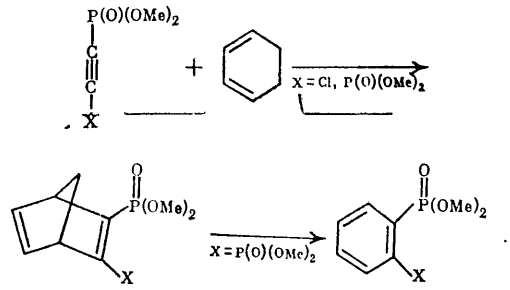


The interaction of ethylthioethynylphosphonate with ethanethiol in the absence of a basic catalyst and under the influence of ultraviolet light leads to the formation of a mixture of isomeric compounds in which 1,2-di(ethylthio)-vinylphosphonates predominate, which indicates a free-radical reaction mechanism[12]:

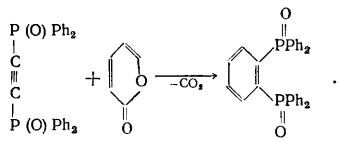


Ethynylphosphonates are reactive in diene synthesis and 1,3-dipolar cycloaddition reactions. Dimethyl chloroethynylphosphonate and tetramethyl acetylenediphosphonate interact with cyclohexa-1,3-diene to form norbornadiene

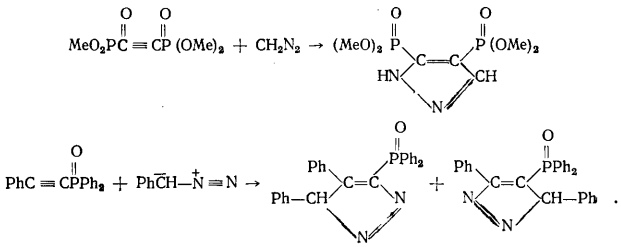
derivatives; in the second case the reaction can be completed by the formation of *o*-bis(dimethylphosphono)-benzene[11]:



The reaction of bis(diphenylphosphinyl)acetylene dioxide with dihydropyran-2-one leads to an analogous result[14]:



Diazoalkanes add to ethylidyne diphosphonate and diphenyl(phenylethynyl)phosphine oxide[14,16]. The second reaction proceeds non-regiospecifically:

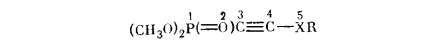


Pudovik, Khusainova, and co-workers investigated a series of reactions involving 1,3-dipolar addition to ethynylphosphonates, established the regiospecificity of the reaction and the dipolar activity of the triple bond as a function of the substituents at the phosphorus atom, and analysed the reaction mechanism within the framework of the molecular orbital perturbation theory. These and other studies of dipolar addition to ethynylphosphonates have been described in a review[47].

Thus ethynylphosphonates undergo all typical reactions characteristic of compounds with an activated triple bond.

IV. THE ELECTRONIC STRUCTURE AND PHYSICAL CHARACTERISTICS OF ETHYNYLPHOSPHONATES

Quantum-chemical calculations in terms of the CNDO/2 approximation indicate the following distribution of effective charges in model ethynylphosphonates[17]:



XR	1	2	3	4	5
H	0.469	−0.256	−0.141	0.010	0.060
Cl	0.450	−0.221	−0.135	0.088	−0.047
SCH_3	0.439	−0.224	−0.127	0.020	−0.018

In the infrared spectra of ethynylphosphonates, the $\nu(C\equiv C) = 2175-2180\ cm^{-1}$ stretching vibration band corresponds to the triple bond and there is an absorption band due to the P=O group at 1240–1270 cm^{-1}. The ^{31}P NMR spectra of ethynylphosphonates show that the phosphorus atom attached to the triple bond resonates in the region of a strong field (from −8 to 10 p.p.m. in alkyl-, chloro-, bromo-, and alkylthio-ethynylphosphonates), undergoing slight downfield displacement in the presence of electron-donating substituents at the triple bond (−3.5 to −3.7 p.p.m. in alkoxyethynylphosphonates and −2.8 to −2.2 p.p.m. in dialkylaminoethynylphosphonates). In ethylnylphosphine oxides the resonance of the ^{31}P nuclei is observed in the range +7 to +9 p.p.m. (relative to 85% H_3PO_4).

The chemical shifts of the acetylenic carbon atoms in the ^{31}C NMR spectra of ethynylphosphonates vary with the substituents at the phosphorus and C(2) carbon atoms. These signals can be readily identified because of the significant difference between the $J_{^{13}C}$ and $J_{^{31}P}$ constants. 2-Hetero-substituted ethynylphosphonates are characterised by the following ^{13}C NMR parameters[12,17]:

Compound	$\delta_{C(1)}$	$\delta_{C(2)}$	$J_{C(1)-P}$	J (—P)
$(CH_3O)_2P(O)C{\equiv}CBr$	54.04	75.88	302.4	56.6
$(EtO)_2P(O)C{\equiv}CCl$	57.49	74.56	300.3	56.7
$(MeO)_2P(O)C{\equiv}CCl$	66.71	62.15	296.7	52.0
$(EtO)_2P(O)C{\equiv}CSEt$	82.40	90.00	284.0	71.3
$(PrO)_2P(O)C{\equiv}CNMe_2$	48.01	63.89	320.2	39.1

Ethynylphosphonates are characterised by considerable electrical dipole moments. Analysis based on an additive scheme indicates the polarisation of the system, which induces the appearance of an additional contribution of 0.7–1.0 D directed towards the phosphorus-containing group[48,50].

Halogenoacetylenes with a halogen atom at the triple bond and particularly those containing unsaturated or aromatic groups or a heteroatom as the second substituent in the ethynyl group undergo the Arbuzov rearrangement with formation of ethynylphosphonates. This reaction constitutes the most general method of synthesis of a wide variety of hitherto inaccessible highly unsaturated phosphorus compounds. The rearrangement involving dihalogeneoacetylenes, which leads, depending on the conditions, to the formation of acetylenediphosphonates or halogenoethynylphosphonates, is of special interest. The latter phosphonates are capable of participating in halogen substitution reactions with retention of the triple bond.

The reactions of ethynylphosphonates with participation of the triple bond make it possible to synthesise a wide variety of unsaturated and saturated functional derivatives of organophosphorus compounds.

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