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2-Cyanoacrylates as Reagents in Heteroatomic Synthesis (A Review)

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ABSTRACT

*Several types of addition reactions to the C=C bond of alkyl 2-cyanoacrylates, $CH_2=C(CN)COOR$ (**1**), are considered. The first examples deal with addition of CH-Acids ($\mathbf{pK}_a$ less than 13) and of H_2S in the presence of catalytic amounts of strong amines, also of mercaptans, thiocarboxylic, and thiophosphoric acids. P-Sulfenylchlorides and acidic phosphites add irreversibly at 20°C to form addition products in accordance with the distribution of charges in **1**. HCl reversibly adds to **1** and to the acid chloride $CH_2=C(CN)COCl$ (**2**). Alcohols and H_2O also add reversibly to the acid $CH_2=C(CN)COOH$ (**3**) and to esters of **1** to transform **1** and **3** into polymers. Triethylsilane in the presence of CF_3COOH (**4**) reduces the C=C bond of **1** and **3** to the corresponding saturated derivatives.*

*The second set of examples involves reactions of **1** with P-III compounds in the presence or absence of **4**. Ph_3P as well as other weak nucleophiles reversibly add to **1** in the absence of **4** to cause instant polymerization. However, **4** protonates an initially formed zwitter-ion in the reaction of **1** with Ph_3P,$(EtO)_3P$,$(EtO)_2PCl$,Ph_2PCl and thiourea to afford stable addition products. IR spectroscopy reveals the formation of H-complexes of **4** with the CN and COOR groups of **1**, which stimulates the addition of the weak nucleophile $(o\text{-}C_6H_4O_2)PCl$ to the C=C bond of **1**. This reagent does not react with **1** in the absence of **4**. Strong nucleophiles, Alk_3P, and $(Et_2N)_3P$ in excess irreversibly add at 20°C to **1** to form zwitterions, which specifically react with PhN=C=O to give stable products. 1,3,2-Dioxaphospholes react with **1** either to form spirophosphoranes or 2-cyano-3-phosphoranylpropionates.*

INTRODUCTION

2-Cyanoacrylates $CH_2=C(CN)COOR$ (**1**) were first made available about 45 years ago, and, for almost 40 years, the chemistry of this type of compound has involved only polymerization reactions that occur extremely easily via an anionic mechanism under the influence of different nucleophiles, and also metals and traces of water, rubbers, plastics, glasses, metal salts, etc. [1]. These unique properties formed the base for application of **1** as cold-curing adhesives. At present, these adhesives are manufactured by a variety of firms in the United States, Germany, Japan, and other countries. Judging by the patent data, the industrial method for manufacturing **1** is based on the Knoevenagel reaction between cyanoacetic acid esters and paraformaldehyde under the influence of different catalytic systems. At an early stage, an oligomer is formed. At a later stage of the process, the oligomer is thermally transformed into the monomeric ester **1**.

It is of interest that the adhesive effect of **1**, originating in the polymerization, occurs only between the surfaces to be glued. The polymer prepared separately does not possess adhesive properties at temperatures under room temperature.

The statement about the extremely high tendency to instant polymerization effected by different compounds has led to a paradoxical fact that, for more than 40 years, the monomeric chemistry of **1** was neglected, and only a few esters have been explored with respect to their chemical reactivity

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Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

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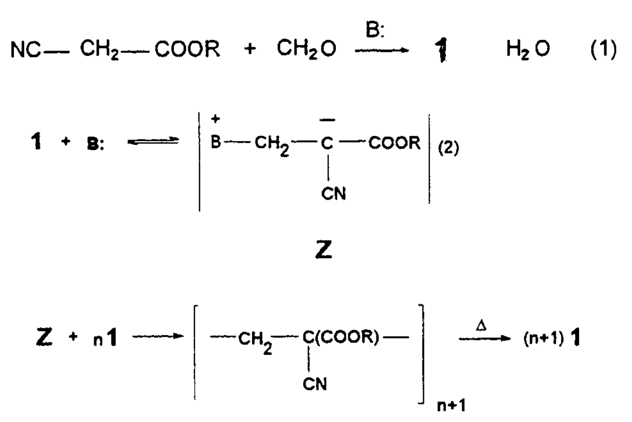


SCHEME 1

among the derivatives of 2-cyanoacrylic acid. Even 2-cyanoacrylic acid (before the patent of 1985 [2]) and its derivatives were not evaluated, and there have been no data on the reactivity of the CN and COOR groups published. Involvement of the C=C bond in reactions with nucleophiles led only to polymeric products. (However, the anthracene adducts for the synthesis and purification of **1** had been reported in 1978 [3]). At the end of the 1980s, in our laboratory, ideas were developed that allowed us to overturn the existing opinion about the impossibility of the involvement of **1** in uncomplicated organic and organoelement synthesis [4]. This review includes information from many publications showing the broad application of 2-cyanoacrylates in organic and heteroatomic synthesis.

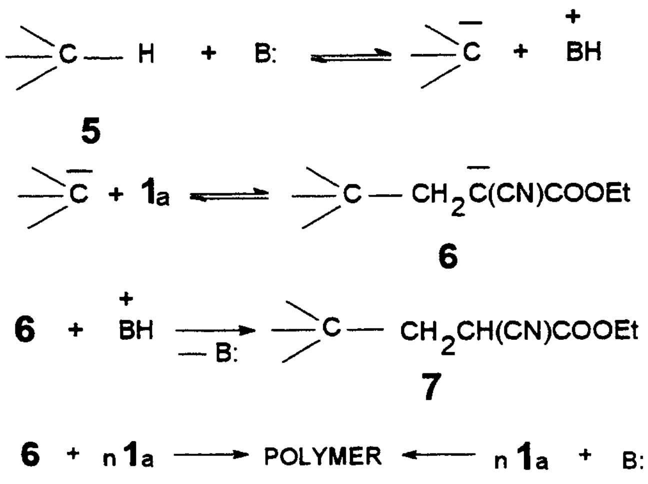
Molecule **1** has three characteristic reactivity centers: a highly electrophilic C=C bond, an alkoxycarbonyl group, and a nitrile group. All three groups strongly influence each other, because they are closely situated. Two highly electron-withdrawing groups (CN, COOR) confer high electrophilicity on the β-carbon atom of the C=C bond; the nitrogen of the cyano group has a reduced nucleophilicity (for example, ethyl 2-cyanoacrylate does not react with PCl_5 in benzene or CCl_4 solution), and 2-cyanoacrylic acid is a rather strong acid [5]. The carboxy and nitrile groups are in conjugation with the C=C bond.

The most interesting results at the present time are connected with the reactivity of the C=C bond in **1** toward different nucleophiles.

In connection with the fact that the chain growth rate in an anionic polymerization is very high [6], we reasoned that, to attain a monomeric reaction product, it is necessary to control at least two conditions:

(1) a minimal amount of a free 2-cyanoacrylic acid ester must be present in the reaction mixture at any moment; and

(2) a primary addition product must be formed at a high rate, and it either must be rather stable or conditions for its stabilization must be created. The latter means in a practical sense that an anionic center at the α-carbon of the primary reaction product **Z** must be trapped instantly (Scheme 1).



SCHEME 2

ADDITION OF CH-ACIDS TO 1A (R=Et) *UNDER MICHAEL REACTION CONDITIONS*

Nitrogen bases cause instant polymerization of 2-cyanoacrylates under any order of mixing of the reagents. This is accounted for by the fact that the equilibrium (Scheme 1, line 2, B = amine) is significantly shifted to the left, and therefore, at any moment (even under very slow addition of **1a** to an amine), there is a sufficient amount of the 2-cyanoacrylate in the reaction mixture to react with the initially formed anion **Z** so that, at a high rate, it is transformed into a polymer.

In fact the authors [7] managed to carry out the Michael reaction and to bring about the addition to the C=C bond of **1a** only those CH acids, **5**, the reaction rate of which with amines significantly exceeds that for the reaction of amines with 2-cyanoacrylates (Scheme 2).

By this criterion, strongly basic amines react with rather strong CH acids (p*K* not exceeding 13–14), to convert CH acids into the conjugate bases. The latter react with **1a** to generate the anion **6**, which may, in principle, be either protonated to give the Michael reaction product **7** or react with a 2-cyanoacrylate to give rise to a polymerization process. The direction of the process—polymerization or formation of the addition product **7**—is determined by the balance of CH-acid acidity, basicity of the amine, electrophilicity of **1a**, and the nature of the solvent.

It turned out that ethyl 2-cyanoacrylate (**1a**), in the absence of bases, does not react with nitroace-

TABLE 1 Dependence of the Yield of the Adduct of Ethyl 2-cyanoacrylate **7** and Polymer on the CH-Acid Acidity in the Presence of Piperidine (5%) (Acetonitrile, 20°C)

CH Acids	*pK$_a$ (5), DMSO*	*Yield % 7*	*Yield % Polymer*
5a	9.0	90.0	0.0
5b	12.8	85.0	0.0
5c	14.2	66.0	10.0
5d	15.0	15.0	80.0
5e	16.7	0.0	100.0

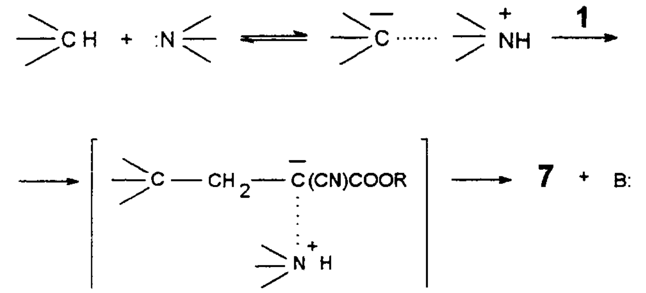
TABLE 2 Compounds **7**

	B.p., °C/Torr	*Note*
O_2N-CH(COOEt)-CH_2-CH(CN)COOEt	156–157/$_{0.5}$	unknown
NC-CH(COOEt)-CH_2-CH(CN)COOEt	150–151/$_{0.5}$	Ref. [8]
MeC(O)-CH(COOEt)CH_2-CH(CN)COOEt	142–144/$_{0.5}$	unknown

tic **5a**, cyanoacetic **5b**, acetoacetic **5c**, or malonic esters **5e**; **1a** also does not react with nitromethane **5d** under these conditions. However, addition to the above-mentioned mixtures of a 5% solution of a strongly basic amine in acetonitrile at 20°C leads to a fast reaction, and, depending on the basicity of the amine used and the strength of the CH acid, an adduct **7** and a polymer of the 2-cyanoacrylate are formed in different ratios. By comparisons based on the use of the same amine, it can be seen clearly (Table 1) that the yield of the adduct **7** increases with increasing CH acidity, while the use of weaker CH acids leads to polymerization of **1a**.

Similar results are obtained by using other strong amines (triethylamine, *tert*-butylamine). However, the use of less basic amines—aniline, pyridine, *N*-methy-laniline—which less readily deprotonate the CH acids mentioned, cause only polymerization of the 2-cyanoacrylates.

A question arises as to why the carbanion, originating from a strong CH acid and a strongly basic amine (**B**:) does not cause polymerization of the 2-cyanoacrylate even if there is a sufficient amount of the latter available under the conditions of the experiment. It is quite evident that, if the anion **6** were an independent entity in the reaction mixture, it would combine with a 2-cyanoacrylate molecule and cause a subsequent polymerization of the latter. Therefore, it is logical to suppose that, in a nonaqueous medium, a carbanion **6** exists mainly as an ion pair with the conjugate acid of the amine (Scheme 3), and reacting with **1** in a cage of solvent molecules, the adduct of the anion with the acrylate undergoes protonation, thus causing no polymerization of the excess of **1** [7].



SCHEME 3

Thus, the Michael reaction involving 2-cyanoacrylates is a general way for preparing esters of substituted 2-cyanocarboxylic acids. Probably, any CH acid with p*K* = 13 or less might successfully be involved in the reaction with **1** in the presence of triethylamine or any other strong organic base (Table 2).

Compounds of the type Et_3SiH, unlike CH acids, cause instant polymerization of 2-cyanoacrylates. However, in the presence of CF_3COOH, reduction of the C=C bond takes place [9] (Scheme 4).

Employment of the D-derivative, Et_3Si-D in the reaction with **1a** leads to the ester CH-D-CH(CN)COOEt **8b**. Reactions leading to **1a** and **3** may be depicted in a general way by Scheme 5.

REACTIONS OF 2-CYANOACRYLATES WITH HETEROACIDS

Heteroacids show a somewhat different reactivity towards 2-cyanoacrylates; such reactions may be

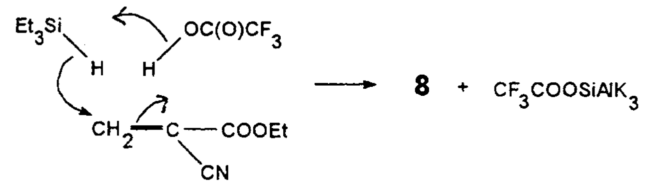
$$\mathbf{1a}\ \xrightarrow[CF_3COOH]{Et_3SiH} CH_3CH(CN)COOEt$$

8

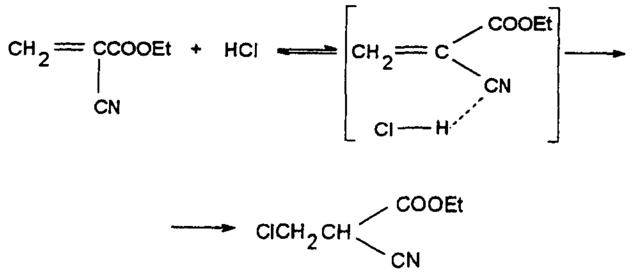
$$\mathbf{3}\ \xrightarrow[CF_3COOH]{Et_3SiH} CH_3CH(CN)COOSiEt_3$$

8a

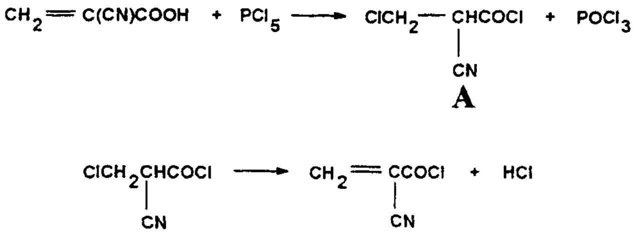
SCHEME 4



SCHEME 5



SCHEME 6



SCHEME 7

subdivided into the following groups, depending on the acid type:

(1) weak acids with a weakly nucleophilic conjugate anion;
(2) strong acids with a weakly nucleophilic conjugate anion;
(3) strong acids with a highly nucleophilic anion; and
(4) weak acids with a highly nucleophilic anion.

Reactions of 2-cyanoacrylates with the aforementioned heteroacids are being investigated, and we can make some generalizations.

Weak acids with a weakly nucleophilic anion are quite inert toward 2-cyanoacrylates, and no sign of reaction between acetic acid and the functional groups of 2-cyanoacrylic acid esters, for example, have been detected. However, strong acids with a weakly nucleophilic anion (for example, CF_3COOH) form H bonds both with CN and probably with COOEt groups in $CHCl_3$ solution, as detected by IR spectroscopy [10] (Scheme 6).

An easily explained sequence of reactions arises on contact of 2-cyanoacrylates with strong acids having a highly nucleophilic anion. In this case, the formation in the first stage of a hydrogen bond with nitrogen of the cyano group and then the addition of an anion to the beta position of the C=C bond takes place. For example, hydrogen chloride in a CCl_4 solution, according to IR spectroscopic data, forms a pronounced hydrogen bond with the CN group [10], while, according to ^{1}H NMR data, the contact results in the formation of a protonic system ABX. As expected, the primary protonation of the cyano group (or the ester group) promotes the addition of the anion (Scheme 6).

Addition of hydrogen chloride is reversible and its adduct with ethyl 2-cyanoacrylate decomposes when heated. A similar reactivity pattern was observed in the preparation of the acid chloride of 2-cyanoacrylic acid from 2-cyanoacrylic acid and PCl_5 [5] (Scheme 7).

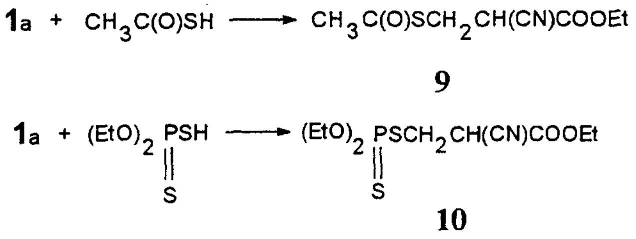
In this case, the adduct **A** initially formed in the reaction can be detected; it decomposes in vacuum.

More stable adducts are formed in the reactions of ethyl 2-cyanoacrylate (**1a**) with carbon thioacids and with phosphorus thioacids [4] (Scheme 8). In these cases, the reaction products can be isolated by distillation in a vacuum.

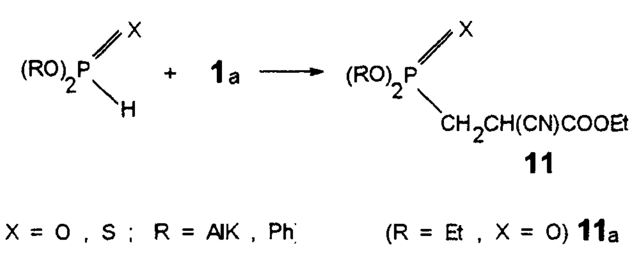
Acid phosphites can add to **1a** at 80°C without the presence of bases [11] (Scheme 9).

Adducts **9–11** decompose into the starting compounds only in a basic medium, initiated by the abstraction of an active alpha-H atom by the base (Scheme 10).

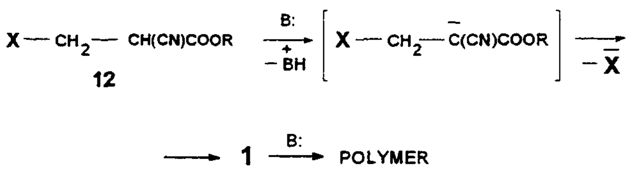
It is possible to obtain from **1** thiolphosphates containing a thiophosphate group in the alpha position to the carboxy group (Scheme 11). In this



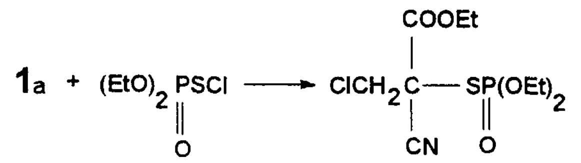
SCHEME 8



SCHEME 9



SCHEME 10



SCHEME 11

$$1a + RSH \longrightarrow RSCH_2CH(CN)COOEt$$

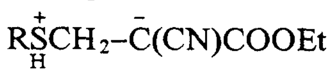
SCHEME 12

case, it is necessary to use a *P*-sulfenylchloride in reaction with a 2-cyanoacrylate [12].

A highly electrophilic carbon in ethyl 2-cyanoacrylate unambigously orients the addition of a *P*-sulfenylchloride to afford only the one regioisomer.

Highly nucleophilic mercaptans have a rather active hydrogen atom and easily and quantitatively add to the C=C bond in **1a** without basic or acidic catalysts [4] (Scheme 12).

The adducts are stable liquids under neutral conditions. To obtain these compounds, it is necessary to carry out a slow addition of **1a** to the mercaptan. Owing to the fact that the reaction rate is very high and because the reaction is practically irreversible at 20°C, there is no excess of the 2-cyanoacrylate at any time. (With reverse mixing of the reagents, the initially formed zwitter-ion instantly reacts with **1a** to cause polymerization). The reaction is of a general character, and it successfully proceeds (under mild conditions and quantitatively) with different mercaptans. Even if one follows the reaction rate in dilute solutions with the help of ^1H NMR spectroscopy, it is difficult to arrive at unambigous conclusions about the detailed mechanism. However, relative rates can be determined in a qualitative manner (Scheme 13).



$$R\overset{+}{\underset{H}{S}}CH_2\text{–}\overset{-}{C}(CN)COOEt$$

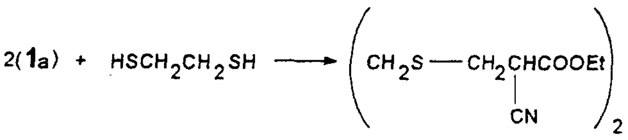
B

A complex mixture of electronic and steric effects influences the reaction rate. Creation of the conditions for radical transformations or the addition of the thiolate anion does not affect the rate of the addition reaction.

Relative reaction rates for the addition of mercaptans to ethyl 2-cyanoacrylate (qualitative comparison).

$$HOCH_2CH_2SH > n\text{-}BuSH > MeC(O)SH > t\text{-}BuSH > PhSH$$

SCHEME 13



SCHEME 14

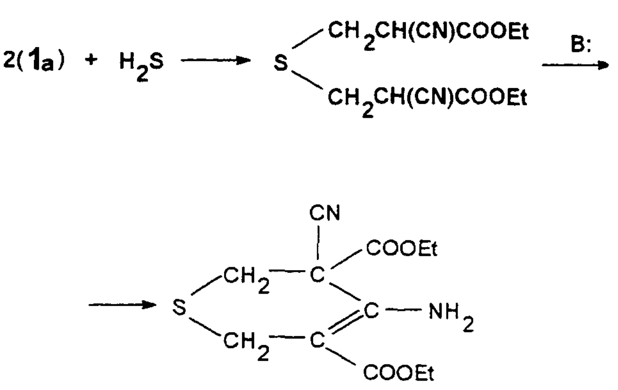
Similarly to monomercaptans, bis-mercaptans easily react with **1a**. Bis-sulfides are obtained [13] (Scheme 14).

Polyaddition involving bis-mercaptans and bis-2-cyanoacrylates [3], affording polymeric products, is also known.

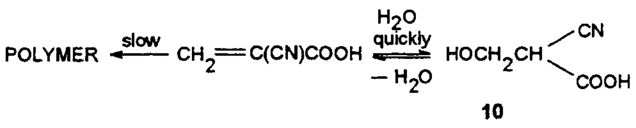
The reaction of ethyl 2-cyanoacrylate with hydrogen sulfide [13] occupies a unique place in the spectrum of reactions between **1** and sulfhydryl compounds. Ethyl 2-cyanoacrylate **1a** was found to react vigorously with hydrogen sulfide under the influence of microamounts of triethylamine, the role of which is not yet quite clear. Possibly, triethylamine catalizes the reaction via transformation of the H_2S molecule into its thiolate-anionic form, or, which is more probable, catalytic amounts of triethylamine are necessary at the second stage of the reaction, a Thorpe-Ziegler cyclization affording a six-membered heterocyclic compound (Scheme 15).

In contrast to mercaptans and hydrogen sulfide, their oxygen analogs, alcohols and water, do not form stable adducts with ethyl 2-cyanoacrylate under similar conditions. However, their formation is detected spectroscopically. Thus, 2-cyanoacrylic acid, **3**, when dissolved in water is transformed into a hydrated derivative, **10**, which is thermodynamically unstable, and gradually is transformed into a polymeric gel of 2-cyanoacrylic acid [5] (Scheme 16).

In the adduct **10**, the methyne hydrogen atom is easily replaced by deuterium with the help of D_2O, which transforms a complex multiplet (ABC) in its NMR spectrum into a quartet, corresponding to the (AB) system. Similarly, in the ^1H NMR spectra, signals are revealed for the hydrogen atoms of



SCHEME 15



$$\text{POLYMER} \xleftarrow{\text{slow}} CH_2{=}C(CN)COOH \underset{-H_2O}{\overset{H_2O}{\underset{\text{quickly}}{\rightleftharpoons}}} \underset{\mathbf{10}}{HOCH_2CH(CN)COOH}$$

SCHEME 16

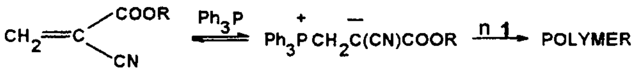
the adduct **11** on dissolving ethyl 2-cyanoacrylate in an organic solvent in the presence of alcohols and sulfur dioxide (Scheme 17).

Without the presence of sulfur dioxide, the mixture is transformed into a polymeric gel. It should be pointed out that, in an earlier publication, a 2-cyano-3-methoxybutyric acid ester **12** was described [14]. The latter was prepared by another method (Scheme 18), and it is probably very unstable (yield of **12** being about 7%).

REACTIONS OF 2-CYANOACRYLATES WITH TRIVALENT PHOSPHORUS COMPOUNDS

Nucleophilic properties of trivalent phosphorus compounds are known to vary broadly, from PCl_3, which for all practical purposes does not display nucleophilicity, to trialkylphosphines, some of the strongest nucleophiles in heteroatom chemistry.

In reactivity toward 2-cyanoacrylic acid esters, trivalent phosphorus compounds can be divided into three groups. The first one includes PCl_3 and similarly low nucleophilic phosphorus halides (type $(o\text{-}C_6H_4O_2)PCl$), which display no affinity for 2-cyanoacrylates at 20°C. The second type of trivalent phosphorus compounds includes weak nucleophiles, which, at room temperature, reversibly add to 2-cyanoacrylates, but the equilibrium is so highly shifted to the left that, under any conditions of the experiment, it is impossible to create a deficit of 2-cyanoacrylate in the reaction mixture. As a result, the reaction leads to an instant polymerization involving the phosphonium center as the head group of the polymer that is formed (Scheme 19).

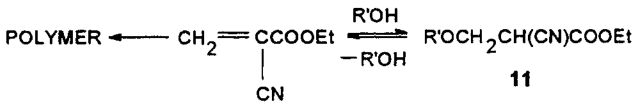


$$CH_2{=}C(COOR)(CN) \underset{}{\overset{Ph_3P}{\rightleftharpoons}} Ph_3\overset{+}{P}CH_2\overset{-}{C}(CN)COOR \xrightarrow{n\,\mathbf{1}} \text{POLYMER}$$

SCHEME 19

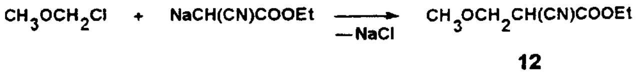
The third group of P(III) nucleophiles includes strong nucleophiles, which react with 2-cyanoacrylates at such a high rate that, under slow addition of a dilute 2-cyanoacrylate solution to, for example, a trialkylphosphine or $(Et_2N)_3P$, one can create conditions under which polymerization of the 2-cyanoacrylate is minimal and major, stable reaction products that are the zwitter-ions **13–15** [15] (Scheme 20) being obtained.

It is necessary to point out that these zwitter-ions, when placed in a 2-cyanoacrylate solution, cause instant polymerization to occur. IR spectroscopic studies of zwitter-ions **13–15** testify to a high delocalization of the negative charge over the carboxy and nitrile groups [15]. In this respect, the structure of the anionic part of the zwitter-ions **13–15** is analogous to that of sodium salts of cyanoacetic acid esters [16]. It might be supposed that the chemical properties of zwitter-ions **13–15** would be analogous to those of the sodium salts of alkyl cyanoacetates. However, the zwitter-ions actually show a sharp difference in behavior, because they exist in a benzene solution as intimate ion pairs. And, due to a high affinity of phosphorus for oxygen, an intramolecular contact of the cationic center of the zwitter-ion and the carbonyl oxygen of its anionic part exists. These structural pecularities, in fact, alter their chemical properties. Thus,



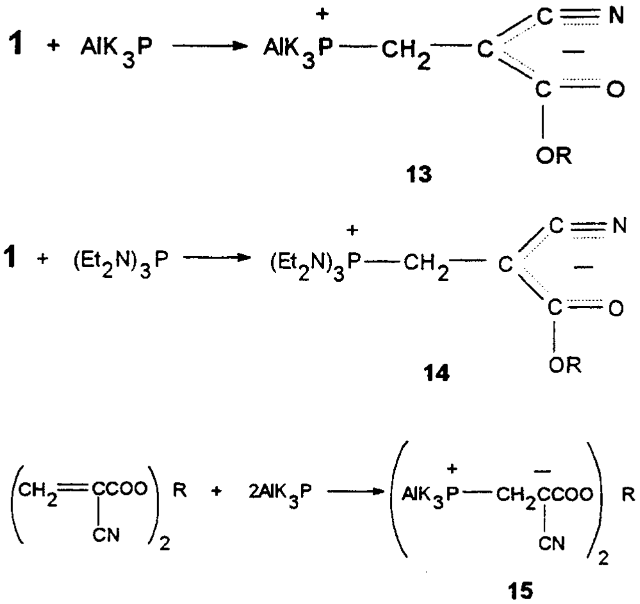
$$\text{POLYMER} \longleftarrow CH_2{=}C(CN)COOEt \underset{-R'OH}{\overset{R'OH}{\rightleftharpoons}} \underset{\mathbf{11}}{R'OCH_2CH(CN)COOEt}$$

SCHEME 17



$$CH_3OCH_2Cl + NaCH(CN)COOEt \xrightarrow[-NaCl]{} \underset{\mathbf{12}}{CH_3OCH_2CH(CN)COOEt}$$

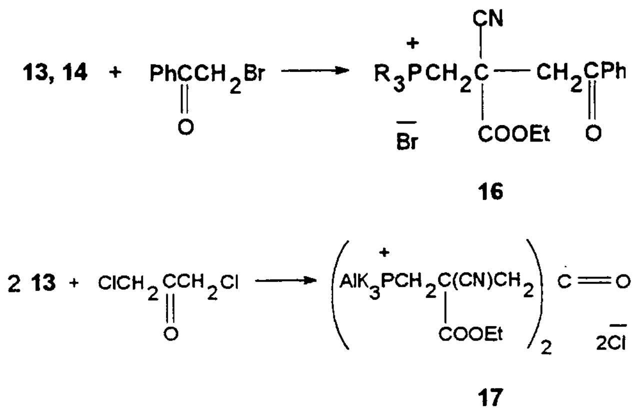
SCHEME 18



$R{=}(CH_2)_n$, where n=8,10

Alk=Pr, Bu

SCHEME 20



SCHEME 21

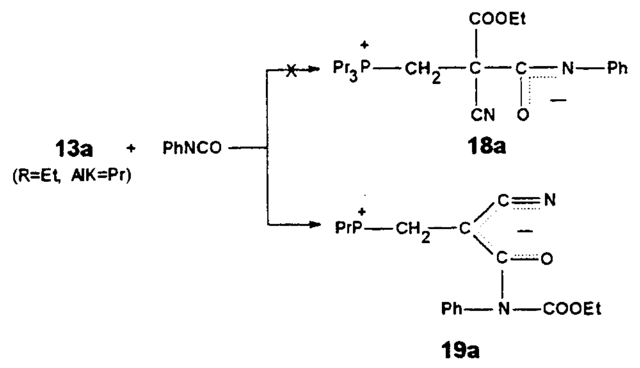
alkylation of zwitter-ions with alkyl halides of either a complex or a simple structure leads usually to C-alkylation, as shown in Scheme 21 [17].

The reaction of a zwitter-ion with an electrophile that lacks a good leaving group, PhN=C=O for example, affords, not the expected adduct **18a**, but the isomeric zwitter-ion **19a** [18] (Scheme 22).

The molecular structure of the compound **19a** is shown in Fig. 1. Details will be published elsewhere [19].

One can suppose that a rearrangement of the primary adduct **18a** into the zwitter-ion **19a** proceeds via an unstable phosphorane **20**, the formation of which is stimulated by the positively charged phosphorus and the inclusion of the phosphorus into a five-membered ring (Scheme 23).

The mechanism of the novel reaction shown in Scheme 23 requires further investigation, but the possibility of the intramolecular phosphorylation of the carboxyl oxygen in the betaines of type **13** has been shown by us experimentally [20]. Thus, inclusion of phosphorus into a five-membered ring by the formation of a covalent bond between phosphorus and the oxygen of a carboxy group of an intermediate zwitter-ion **22** is shown in Schemes 24 and 25.



SCHEME 22

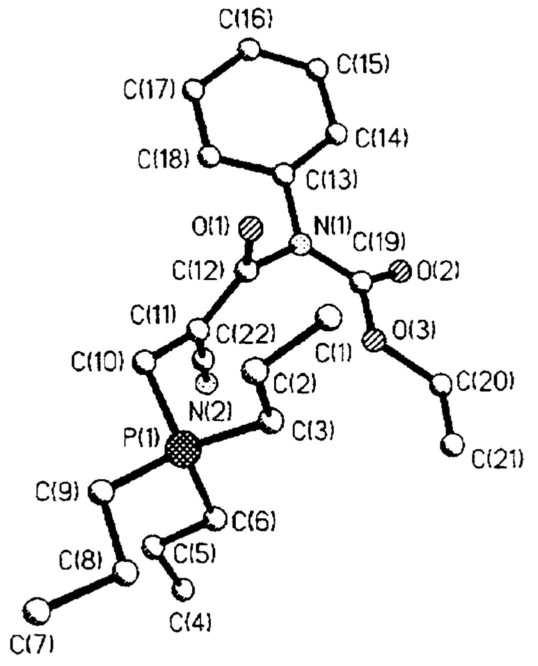
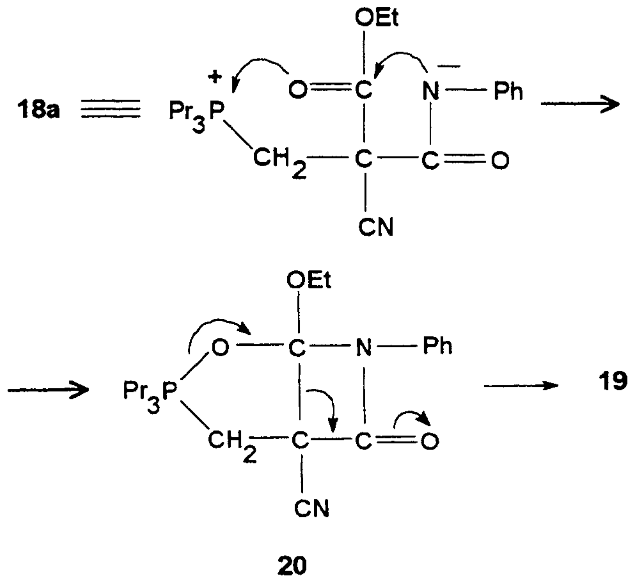
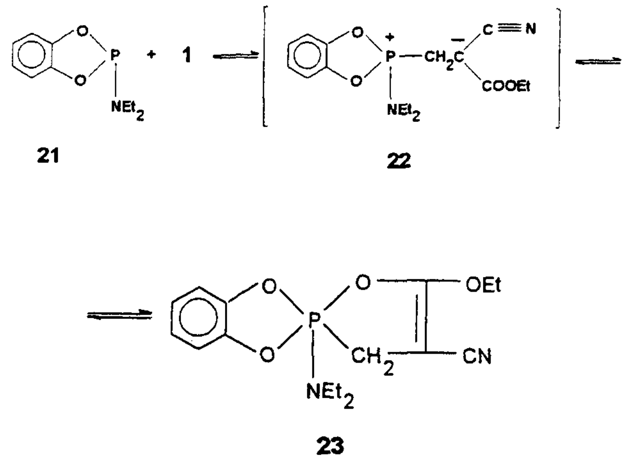


FIGURE 1 Molecular structure of the compound **19a**.

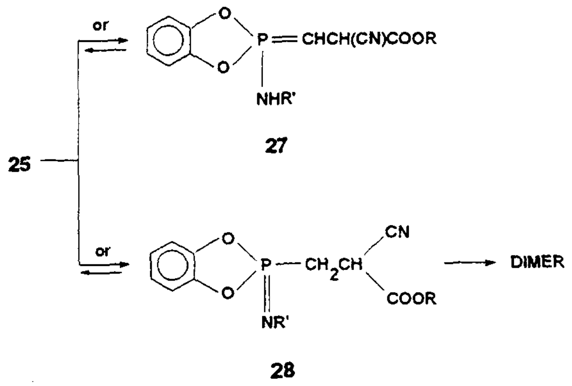
Thermodynamic stability of spirophosphoranes **23** and **26** depends on steric and electronic characteristics of the starting phosphorus P(III) derivatives. For example, the zwitter-ions **13**–**15** are quite stable at 20°C. They do not cyclize to a spirophosphorane, and they do not decompose to the starting compounds. However, as shown in Scheme 24, the formation of spirophosphorane **23** is controlled by kinetic factors. According to ^1H NMR and IR spectroscopic data, on mixing ethyl



SCHEME 23



SCHEME 24



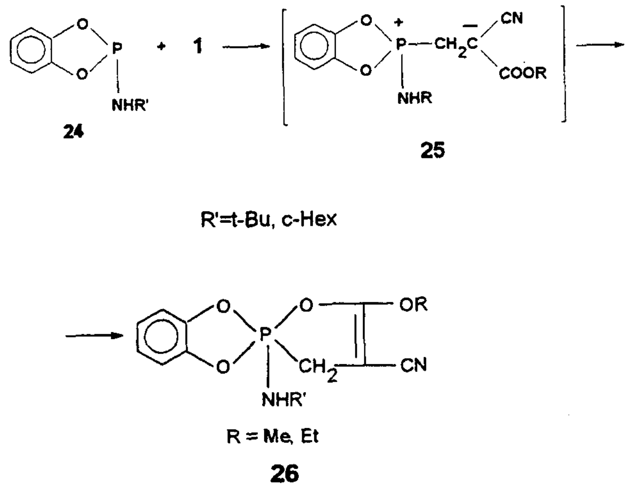
SCHEME 26

2-cyanoacrylate with compound **21**, spirophosphorane **23** is formed immediately, and its lifetime is several hours. By the next day, however, ^{31}P NMR spectroscopy detects the signal of the starting compound **21**, and ^{1}H NMR spectroscopy reveals the formation of a 2-cyanoacrylate polymer.

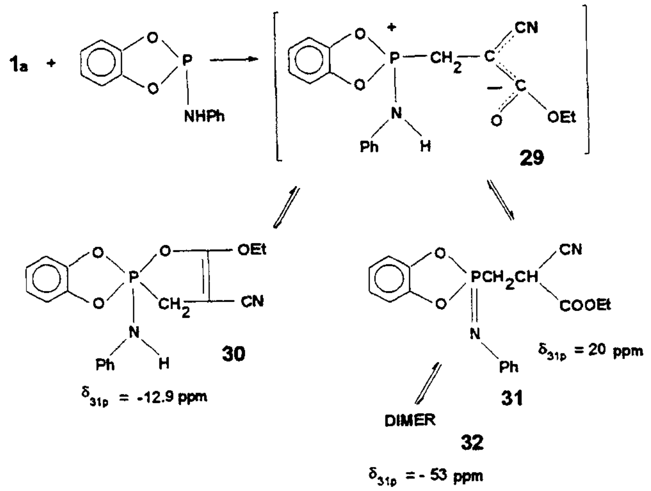
The bonding to phosphorus of a branched primary amine in each compound **26** leads to a stable crystalline spirophosphorane, which is stable up to 80°C, but, at higher temperature, each compound **26** transforms into a mixture of compounds with chemical shifts in the region δ 20–40. This testifies to the retainment of the P-C bond in each compound. As shown in Scheme 26, stabilization of a zwitter-ion of type **25** is possible by the transfer of a proton from the neighboring CH group or a proton from the NH group to the carbanionic carbon.

In the first case, ylide **27** would be formed, and in the next one, an imide **28**. Stabilization by the first route is of small probability, because the basicity of the anionic charge in **25** is so low that a possible equilibrium must be shifted completely to the left. The transfer of a proton from nitrogen to the carbanionic center is more probable, especially if the mobility of the hydrogen of the NH bond is rather high and the configuration of the imine formed is such that its conversion to a more stable dimer is possible. In fact, we managed to reveal by ^{31}P NMR spectroscopy that, on introducing a phenyl group on the nitrogen, the reaction products are compounds with chemical shifts being characteristic not only of a betaine **29**, but also of a phosphorane **30** and a dimer **32** of **31** (cf. [21]) (Scheme 27).

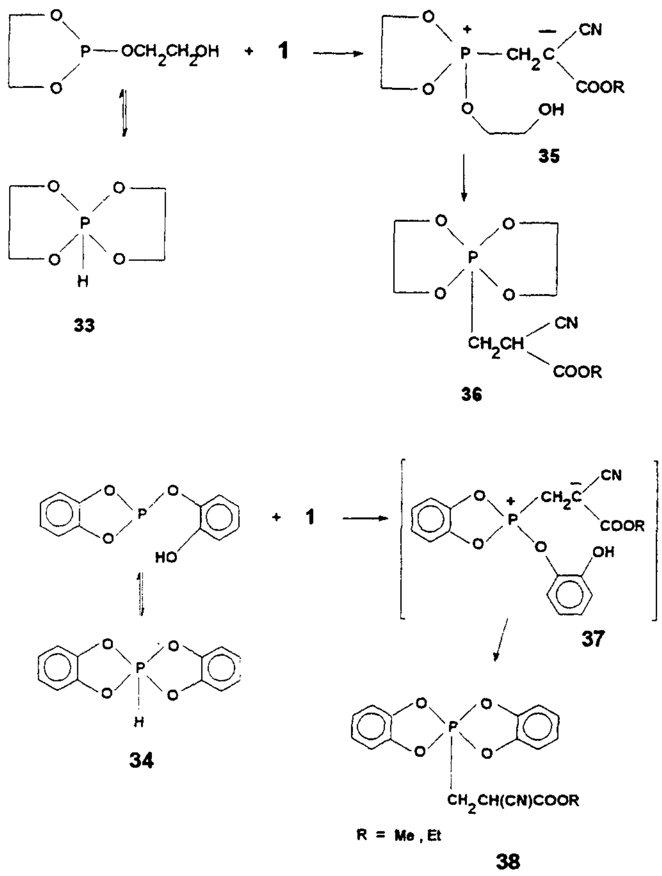
Stabilization of each initially formed zwitter-ion is possible, not only by its intramolecular spirocyclization, but also by "trapping" of the anionic charge by an active hydrogen of each of the starting nucleophiles **33** and **34**, each hydrogen being separated from phosphorus by five bonds. The following Scheme 28 includes the equations for the



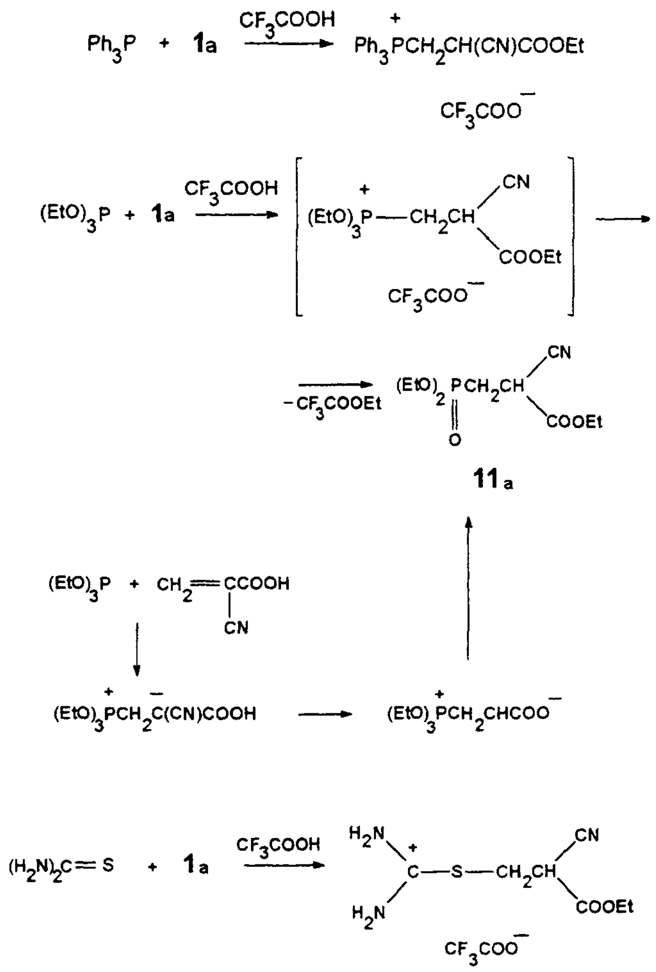
SCHEME 25



SCHEME 27



SCHEME 28



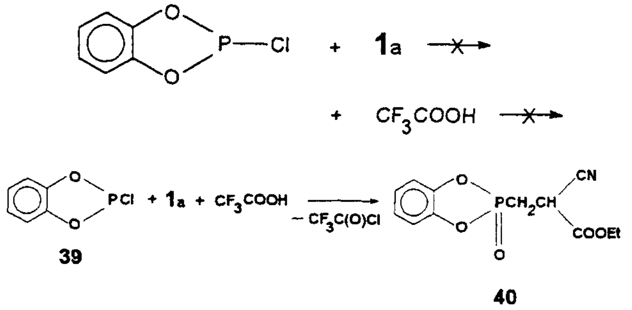
SCHEME 29

reactions between equilibrated mixtures of **1** and **33** with **35** and **36** and of **1** and **34** with **37** and **38**.

It is logical to suppose that, in the first stage, zwitter-ions **35** or **37** are formed. They undergo intramolecular proton transfer and ring closure into a spiro-phosphorane system containing two five-membered rings. Such a way of trapping the anionic charge with the help of an active alcoholic hydrogen proceeds successfully only if the formation of a five-membered ring is possible on transferring a proton to the anionic charge in the zwitter-ion. If the starting phosphite is a trimethylenglycol derivative, the reaction results in a complex mixture of monomeric and polymeric phosphorus-containing compounds.

Trapping of the anionic charge in the initially formed zwitter-ion can be carried out with the introduction of a third reagent into the reaction mixture. This allows a shift in the equilibrium between a weak nucleophile and the 2-cyanoacrylate to the right and to form different derivatives with P-C and S-C [22] bonds, as shown in the respective examples (Scheme 29).

Of special interest is the example of the reaction between a very weak nucleophile **39** and **1a** in the presence of CF_3COOH, affording a phosphonate **40** [25]. It was especially established that, without the presence of CF_3COOH, 2-chloro-1,3,2-benzodioxaphosphole **39** did not react with ethyl 2-cyanoacrylate. The ^1H NMR spectra of an equimolar mixture of the two reagents, recorded at 20°C and −50°C, gave signals of the starting compounds only. It was also detected that compound **39** remained unchanged in the presence of CF_3COOH under the reaction conditions. A possible participation of



SCHEME 30

acidic phosphites that add to the C=C bond can be excluded because, as it turned out, the presence of CF_3COOH prevents such an addition.

Thus, the reaction shown in Scheme 30 is the first example of the conjugate addition of a weak nucleophile to a 2-cyanoacrylate under the influence of acid. The catalytic effect of the acid on the 2-cyanoacrylate evidently relies on the protonation of the CN group, which allows the formation of the phosphorus-carbon bond with the participation of a very weak nucleophile **39**.

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