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2-Cyanoacrylates. Synthesis, properties and applications †

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Contents

Abstract. Methods for the synthesis, properties and applications of alkyl 2-cyanoacrylates are surveyed. The reactions of alkyl 2-cyanoacrylates with various nucleophiles (thiols, alcohols, diols, hydrogen sulfide, phosphines, *etc.*) including a new reaction involving insertion of isocyanates and isothiocyanates into the C=C bonds in the adducts of alkyl 2-cyanoacrylates with trialkylphosphines are considered. The prospects for the use of alkyl 2-cyanoacrylates in organic synthesis, in the chemistry of polymers and in the chemistry of adhesives are described. The bibliography includes 117 references.

I. Introduction

Alkyl 2-cyanoacrylates (ACAs) were synthesised for the first time in 1949;[1] as early as 1955, it was proposed to use these compounds as one-component cold-setting adhesives.[2] Soon after that, industrial production of fast-curing adhesives based on ACAs started, and they appeared on the market.[3,4]

Adhesives based on alkyl 2-cyanoacrylates are unique materials owing to two specific features. The first of them is an extremely short period needed for setting. At room temperature, surfaces can be cemented together with these adhesives over periods of several seconds, high strengths of the adhesive joints being attained fairly quickly. The second feature is that ACAs can efficiently cement together both living tissues (their use in medicine is allowed) or organic materials (plastics, rubber, wood) and inorganic materials (stones, metals, glass, porcelain, ceramics) in various combinations. Apparently, only Teflon and polyethylene provide exceptions; they can be cemented together only after treatment of their surfaces with special activators (amines, phosphines, *etc.*).[5,6]

The ability of ACAs to polymerise instantaneously under the action of traces of water and various compounds (and thus to glue materials together) is the main reason accounting for the fact that up to the beginning of the 90s, only polymeric chemistry of ACAs has developed. In fact, the monographs[3,4] published in 1980 and reviews (see, for example, Refs 7–9) deal mostly with the polymeric chemistry of ACAs. Among monomeric derivatives of 2-cyanoacrylic acid, only esters have been described.

A new stage in the development of the chemistry of ACAs is associated with the synthesis of cyanoacrylic acid (CAA)[10] and the involvement of this acid and its derivatives in organic synthesis.[11,12]

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II. Methods for the synthesis of alkyl 2-cyanoacrylates

Several methods for the synthesis of ACAs (1) are known. One of them is based on the thermolysis of alkyl 3-acetoxy-2-cyanopropionates, which are prepared from the sodium derivatives of the corresponding alkyl cyanoacetates and chloromethyl acetate.[1]

$$MeCOOCH_2Cl + NaCH(CN)COOR \xrightarrow{-NaCl}$$

$$\rightarrow MeCOOCH_2CH(CN)COOR \xrightarrow[-MeCOOH]{\Delta} CH_2{=}C(CN)COOR. \quad 1$$

However, this method has not been adequately studied. The synthesis of the compounds 1 based on the Knövenagel reaction has been developed in greater detail. This method forms the basis for the industrial manufacture of ACAs, as is illustrated by numerous publications.[3,13–29]

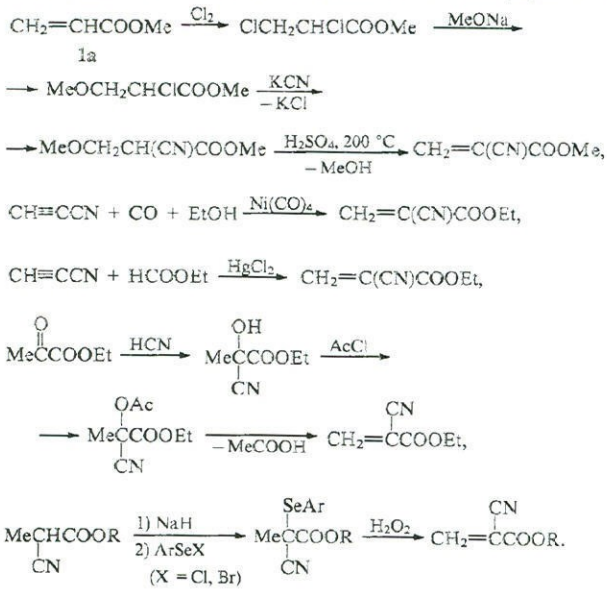
$$n CH_2(CN)COOR + n CH_2O \longrightarrow \left(CH_2-\underset{\displaystyle COOR}{\overset{\displaystyle CN}{\overset{|}{\underset{|}{C}}}} \right)_n \xrightarrow{\Delta} 1.$$

It is noteworthy that depolymerisation of oligomeric ACAs formed in the first stage must be carried out under rather drastic conditions. This fact largely restricts the synthetic potential of this method (for example, it is fairly difficult to synthesise ACAs with bulky ester groups).

Among the methods developed more recently, syntheses of ACAs from methyl acrylate (1a),[30] cyanoacetylene,[31,32] ethyl pyruvate[33] and esters of 2-cyanopropionic acid[34] should be mentioned [apparently, the latter method permits preparation of any ester of 2-cyanoacrylic acid, naturally except for those containing basic groups; the initial esters of 2-cyanopropionic acid can be prepared using both various aliphatic alcohols or phenols and polyols (diols, triols, tetraols) including oligomeric

† The review is dedicated to William E McEwen on occasion of his 75th birthday.

hydroxy-derivatives]. However, to the best of our knowledge, the applications of these methods are limited to laboratory syntheses.



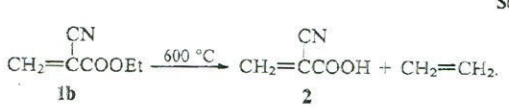
To prevent polymerisation of the ACA formed initially, the anthracene protection of the C=C bond is used. Anthracene is removed subsequently using maleic anhydride.[35-37] This method is labour-consuming; however, it made it possible to solve a fundamental problem, namely, the synthesis of individual bis-2-cyanoacrylates, *i.e.* esters of cyanoacrylic acid and diols.[37]

Now we consider the possible routes for the transformation of commercially available methyl and ethyl cyanoacrylates into other derivatives of cyanoacrylic acid.

Transesterification of ethyl 2-cyanoacrylate with butyl or hexyl alcohols in the presence of acid catalysts has been reported.[38] Evidently, this reaction involves the intermediate formation of an oligomer and its subsequent depolymerisation, because the conditions under which the reaction mixture is treated rule out the existence of a monomeric ACA. The conditions for transesterification of methyl cyanoacrylate with diols permitting the preparation of bis-cyanoacrylates have been given in a patent.[39] However, the target products can be obtained in satisfactory yields only when higher diols are used.

Basically new opportunities for the synthesis of ACAs have appeared in recent years, after the Henkel company had patented thermolysis of ethyl cyanoacrylate (**1b**) as a method for the preparation of free CAA (**2**) (yield 13%, m.p. 80–81 °C) as shown in Scheme 1.[10]

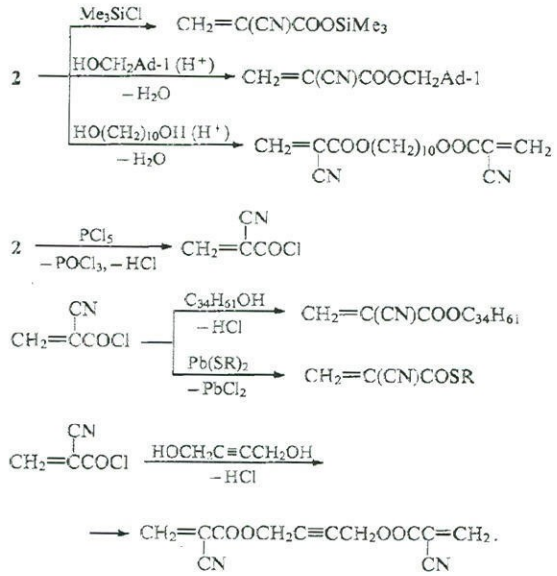
Scheme 1



Although the proposed process was not optimised in this patent,[10] it was shown that the preparation of free CAA is, in principle, possible, and this played an important role in the subsequent development of the chemistry of ACAs. Later, conditions have been found that made it possible to synthesise CAA according to Scheme 1 in yields of up to 60% (the melting point of the compound **2** recrystallised from toluene was 93–94 °C).

The synthesis of free CAA has stimulated the preparation of new derivatives of this acid, first of all, its chloride.[40-44] Direct esterification of CAA or its chloride with complex and bulky alcohols,[41] diols[42-44] or lead thiolates[40] gives rise to CAA derivatives the synthesis of which has previously been difficult or impossible (Scheme 2).

Scheme 2



III. Physical properties of 2-cyanoacrylates

Over the 50 years that have passed after the synthesis of the first alkyl 2-cyanoacrylate, about a hundred compounds of this type have been described. A large group of these compounds comprises ACAs containing residues of complex alcohols:[21,28,34,40,41,43,45-51] for example, esters with double or triple bonds, hinge oxygen bridges, carbonyl or carboxyl groups or chlorine, fluorine or silicon atoms. Esters derived from diols, triols or polyols constitute a separate group.[32,42,44] A few CAA esters derived from thiolates[40] and phenols[34] described recently should also be mentioned.

Whereas cyanoacrylic acid and most of bis-cyanoacrylates are crystalline compounds, the majority of esters of CAA are liquids with boiling points of 50–150 °C (at 0.2–2 mm Hg).

The IR spectra of various ACAs and bis-cyanoacrylates are similar: they contain four characteristic absorption bands at 1600–1640 (C=C), 1720–1750 (C=O), 2260 (CN) and 3100 cm^{-1} (the CH_2 group of the cyanoacrylate fragment).[22] The most characteristic signals in the ^1H NMR spectra of these compounds are those corresponding to the protons in the $CH_2=C(CN)$ fragment (at 6.9 and 7.1 ppm in deuterioacetone or at 5.5 and 6.3 ppm in deuteriobenzene). The ^{13}C NMR spectrum of 2-cyanoacrylic acid (deuterioacetone) exhibits signals for the carbon atoms of the CN (114.9 ppm), C–CN (116.7 ppm), CH_2 (144.1 ppm) and COO (161.3 ppm) groups.

An X-ray diffraction study has shown that the molecule of 2-cyanoacrylic acid is flattened (Fig. 1):[52] the maximum deflection of the non-hydrogen atoms from the mean plane of the molecule

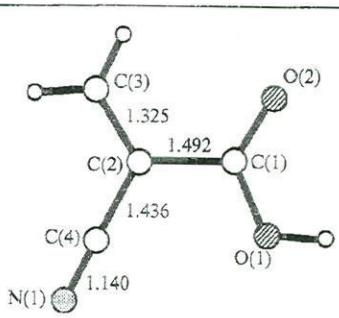


Figure 1. Molecular structure of 2-cyanoacrylic acid.

amounts to 0.150 Å. The C(1)–C(2) bond (1.492 Å) exceeds only slightly the standard C–C distance (1.475 Å); this implies that there is no significant conjugation between the C(1)=O and C(2)=C(3) double bonds (the length of the latter bond also coincides with the typical C=C distance equal to 1.321 Å). The lengths of the C(2)–C(4) and C(4)–N bonds are close to the standard values for molecules incorporating a C=C–C≡N fragment; in this fragment, conjugation apparently does occur.

Strong OH···N hydrogen bonds (1.88 Å) join the molecules into zigzag-like chains of the 'head-to-tail' type. The mutual arrangement of the C=C bonds of neighbouring molecules of the acid does not conform to the necessary conditions for the occurrence of topochemical reactions in the crystals of compounds with double bonds. This is in agreement with the fact that crystals of CAA are resistant to light and to prolonged exposure to X-rays.

1-Adamantylmethyl cyanoacrylate and the bis-cyanoacrylate prepared by transesterification of methyl cyanoacrylate with decane-1,10-diol have also been studied by X-ray diffraction analysis.[43] It was found that the molecular geometries of 1-adamantylmethyl cyanoacrylate and the bis-cyanoacrylate are similar to that of CAA. However, owing to the presence of strong electron-withdrawing groups, the methylene hydrogen atoms in these ACAs are markedly acidic, and this accounts for the short intermolecular contacts involving CH_2 groups in the crystals of these compounds.

It is possible that it is the acidity of the methylene hydrogen atoms that accounts for the ready polymerisation of ACAs in the presence of nucleophiles and bases by virtue of coordination of the latter to the protons of the methylene group of ACAs.

IV. Chemical properties of 2-cyanoacrylic acid and its derivatives

1. 2-Cyanoacrylic acid

As noted above, no reliable data about the existence of free CAA had been reported until 1985. Only Kadykov and Kochkin[53] described the use of CAA (without mentioning the source); however, the procedure presented by these researchers is doubtful.

The presence of the highly electrophilic C=C bond together with the carboxyl and nitrile groups in the CAA molecule accounts for the diversity of its reactions. The preparation of CAA salts is hampered due to the strong tendency of this acid to decarboxylation and polymerisation in the presence of bases. In fact, alkalis, triethylamine and amines with non-branched radicals immediately cause its polymerisation, whereas in the presence of pyridine or diazabicyclooctane, it is rapidly converted into 2,4-dicyanopent-4-enoic acid 4 as shown in Scheme 3.[40]

Scheme 3

$$CH_2{=}C(CN)COOH + B \rightleftharpoons CH_2{=}C(CN)COO^- BH^+ \rightleftharpoons$$

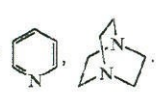
$$\rightleftharpoons {}^+B{-}CH_2C(CN)COOH \xrightarrow[-CO_2]{} {}^+B{-}CH_2\overset{-}{C}HCN \xrightarrow{2}$$

3

$$\rightarrow {}^+B{-}CH_2CH(CN)CH_2\overset{-}{C}(CN)COOH \xrightarrow{H^+}$$

$$\rightarrow CH_2{=}C(CN)CH_2CH(CN)COOH$$

4

B = 

Obviously, in the first stage, an equilibrium is established, *i.e.* in addition to the formation of the salt, an attack by the amine on the highly electrophilic β-C atom occurs. The zwitter-ion 3 resulting from decarboxylation adds to CAA; when the reaction mixture is treated with a solution of sulfuric acid, the adduct is converted into the acid 4 in a high yield. The correctness of this reaction mechanism was confirmed by trapping the anion 3 as the adduct with 4-nitrobenzaldehyde.

$$2 + 4\text{-}O_2NC_6H_4CHO \xrightarrow{Py} 4$$

$$\rightarrow CH_2{=}\overset{CN}{\overset{|}{C}}\overset{OH}{\overset{|}{C}}HC_6H_4NO_2\text{-}4$$

Sterically hindered amines (butyldimethylamine and brucine) react with CAA to give only the corresponding salts, because steric hindrance prevents the attack on the C=C bond.[54] Conversely, in the case of triethyl phosphite, which is less basic but more nucleophilic than amines, the reaction occurs only at the double bond to give compound 5 containing a strong P–C bond.[40]

$$2 + (EtO)_3P \longrightarrow (EtO)_2P(O)CH_2CH(CN)COOEt.$$

5

Nobody has been able yet to prepare the 2-cyanoacryloyl chloride from the acid by exchange reactions that are used successfully to convert acrylic and methacrylic acids into the corresponding chlorides. For example, CAA does not react with benzoyl chloride even at 200 °C. The reaction of CAA with thionyl chloride occurs with difficulty and stops, apparently, at the stage of formation of the mixed anhydride.[40] The chloride of CAA can be obtained only by treating the acid with phosphorus pentachloride in a mixture of toluene with xylene.[40] According to ^1H NMR data, this reaction affords an unstable adduct of the CAA chloride with HCl. When phosphoryl oxychloride and most of the toluene are removed *in vacuo*, hydrogen chloride is eliminated. The solution of 2-cyanoacryloyl chloride thus obtained can be used in various syntheses. For example, ACAs with bulky ester groups[41,43,45] and thioesters of CAA unknown previously have been prepared from 2-cyanoacryloyl chloride. It has been found[33] that, unlike *S*-ethyl cyanothioacrylate which polymerises extremely easily, *S*-*tert*-butyl cyanothioacrylate is fairly stable. To prepare successfully esters of 2-cyanothioacrylic *S*-acid, low-polarity lead thiolate is used, because in the presence of ionic sodium and potassium thiolates, the cyanoacrylate system instantaneously polymerises, evidently, as a result of an attack by the alkali metal thiolate on the β-carbon atom at the double bond.

Like other carboxylic acids, cyanoacrylic acid smoothly reacts with trialkylchlorosilanes[40] to give the corresponding acyloxysilanes in high yields (see Scheme 2).

Unlike acrylic acid, which adds water only at 100 °C in the presence of alkali, CAA, owing to its high electrophilicity, reacts with water at room temperature. This process has been studied using deuterated water.

Hydration of CAA competes with its polymerisation (according to ^1H NMR spectroscopy, the latter reaction occurs much more slowly). Since the process is reversible, 2-cyano-3-hydroxypropionic acid cannot be isolated in a pure state; removal of excess water affords again free CAA and its polymeric form. Thus, the measured pK_a value, equal to 2.3 in a 0.01 N aqueous solution, refers to an equilibrium mixture of CAA with 2-cyano-3-hydroxypropionic acid rather than to CAA itself.[40]

Due to its high reactivity, cyanoacrylic acid forms adducts with acid phosphites and thiophosphites without catalysts,[55] whereas similar adducts of acrylic acid are formed only in the presence of alkaline catalysts.

$$2 + (RO)_2P(X)H \longrightarrow (RO)_2P(X)CH_2CH(CN)COOH.$$

X = O, S.

Cyanoacrylic acid dissolved in dry acetone quantitatively adds ethanedithiol present in excess to give functionally substituted bis-carboxylic acids.[56]

$$2 + HSCH_2CH_2SH \longrightarrow$$

$$\rightarrow HOOC(CN)CHCH_2SCH_2CH_2SCH_2CH(CN)COOH.$$

It is important to follow the order of mixing the reactants in the reactions of CAA (or ACAs). In the above example, as in the reactions with other nucleophiles, it is necessary that a solution of CAA (or ACA) be slowly added to a solution of a nucleophile (desirably, under an atmosphere of dry sulfur dioxide). The opposite order of mixing the reactants causes instantaneous polymerisation of the cyanoacrylate system.

Finally, we mention a fairly unexpected reaction, namely, hydrogenation of 2-cyanoacrylic acid with organosilanes in the presence of trifluoroacetic acid.[57]

$$2 + Et_3SiH \xrightarrow{CF_3COOH} MeCH(CN)COOSiEt_3.$$

The trialkylsilane–trifluoroacetic acid system is known to be efficient for ionic hydrogenation of unsaturated compounds containing electron-withdrawing substituents at the multiple bond. This hydrogenation follows a mechanism that includes protonation of the multiple bond yielding a carbocationic species and subsequent abstraction of a hydride ion from the organosilane molecule. However, in view of the high electrophilicity of the double bond in the CAA molecule, the 'ionic' mechanism of its hydrogenation by silanes should apparently be ruled out. The use of deuterated dimethylphenylsilane showed that deuterium adds only to the β-position of the double bond of the acid.

2. Esters of 2-cyanoacrylic acid

Molecules of ACAs contain three active groups, namely, C=C, C≡N and COOR, which substantially differ in reactivity. The C=C bond is the most reactive of these groups; the β-carbon atom of this bond is rapidly attacked even by weak bases or nucleophiles. The reactions occur at room temperature and are accompanied by anionic 'head-to-tail' polymerisation of ACAs[58] (Scheme 4).

Scheme 4

$$CH_2{=}\underset{CN}{C}COOR + B \rightleftharpoons B{-}\underset{CN}{CH_2C}COOR \xrightarrow{n\,CH_2=C(CN)COOR} B{-}\left(CH_2{-}\underset{COOR}{\overset{CN}{C}}\right)_n CH_2C(CN)COOR$$

(6)

$n > 1$.

Another reaction site in the ACA molecule, *viz.* the nitrogen atom in the cyano-group, possesses low nucleophilicity; therefore, ethyl cyanoacrylate does not react with PCl_5 in benzene even upon prolonged heating of the reaction mixture. However, it has been shown by IR spectroscopy[59] that the proton of trifluoroacetic acid forms an H-complex with the nitrile group of the ACA in a chloroform solution; it will become clear from the following discussion that this increases the electrophilic reactivity of ACAs, so that they can react with weak nucleophiles.

The reactivity of the third reactive site of ACAs, *viz.* alkoxycarbonyl group, has been studied only in relation to transesterification in an acid medium. Using several examples,[39,43] it has been shown that the methoxy-group in methyl cyanoacrylate can, in principle, be replaced by other RO groups; however, transesterification requires elevated temperatures, and, therefore, it is inevitably accompanied by substantial polymerisation of the initial compounds and the products.

a. Reactions of 2-cyanoacrylates with nucleophiles containing no active hydrogen atoms

For the use of ACAs in organic synthesis, studies dealing with their involvement in reactions with various nucleophiles aimed at preparing monomeric compounds are of the greatest interest. Analysis of the experimental data on the reactivities of ACAs towards bases and nucleophiles leads to the following conclusions. The first step in the addition of any base or nucleophile to the double bond of an ACA is reversible. However, the position of the equilibrium is different for various reaction series. For all nitrogen-containing nucleophiles (see Scheme 4), the equilibrium is markedly shifted to the left; hence, the ACA, which is present in the reaction in a substantial amount irrespective of the particular experimental procedure, immediately polymerises *via* consecutive chain growth by an anionic mechanism under the action of zwitter-ion **6** formed initially in the reaction system. Until a paper by Gololobov *et al.*[60] was published, the intermediate **6**, which induces the growth of the polymeric chain, had not been characterised and had not even been detected by spectroscopic methods. It was possible to obtain and isolate intermediate **7** only by using extremely strong neutral nucleophiles like trialkylphosphines and hexaethyl triamidophosphite.[60] Since the reactions of ACAs with these nucleophiles occur at high rates and the equilibrium in the first step shown in Scheme 4 can be completely shifted to the right, high yields of the zwitter-ions **7** were attained. The zwitter-ion **7** obtained from triisopropylphosphine and ethyl cyanoacrylate was studied by X-ray diffraction analysis.[60] The bond lengths in the O(2)–C(3)–C(2)–C(4)–N fragment of the zwitter-ion **7** (R^1 = Et, $R^2 = R^3$ = Pr^i), namely, O(2)–C(3) = 1.123(2), C(3)–C(2) = 1.402(2), C(2)–C(4) = 1.403(2), C(4)–N = 1.156(2) Å, indicate that the negative charge in the fragment is delocalised.

$$R^2_2R^3P + CH_2{=}C(CN)COOR^1 \rightleftharpoons R^2_2R^3\overset{+}{P}{-}\overset{1}{C}H_2{-}\overset{2}{C}\left(\overset{4}{C}{\equiv}N\right)\overset{3}{C}{=}O\,OR^1$$

(7)

R^1 = Me, Et; $R^2 = R^3$ = Pr^n, Pr^i, Bu^n, Et_2N;
R^2_2 = $(CH_2)_4$, R^3 = Et_2N; R^2 = Et_2N, R^3 = Bu^{t}NH.

The delocalisation of the negative charge in the N–C–C–C–O fragment of the zwitter-ions **7** is indicated not only by the bond lengths but also by spectral characteristics of the carboxyl and nitrile groups (Table 1).[61]

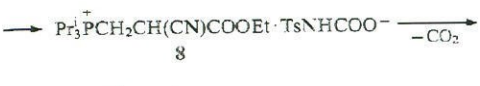
Table 1. Comparison of the IR spectral parameters of zwitter-ions **7** and products of their alkylation.

Compound	ν_{CO}/ cm^{-1}	ν_{CN}/ cm^{-1}
$R^2_2R^3\overset{+}{P}{-}CH_2\overset{-}{C}(CN)COOR^1$ (**7**)	1602–1627	2136–2146 (s)
$Pr^i_3\overset{+}{P}{-}CH_2\overset{-}{C}(CN)C(O)NRCOOEt$ (**11**)	1592, 1690	2158 (s)
$R^2_2R^3\overset{+}{P}{-}CH_2C(CN)(COOEt)R\ X^-$	1730–1745	2241–2256 (w)

For comparison, spectral parameters of the products of alkylation of the zwitter-ions **7** are also presented in Table 1. The absorption frequencies observed for these compounds are standard, because their molecules incorporate no anionic sites capable of being conjugated with the CN and COOR groups.

Under certain conditions, the zwitter-ions **7** form molecular compounds with toluene-*p*-sulfonylamide.[62] For example, the reaction of zwitter-ion **7** with toluene-*p*-sulfonyl isocyanate in wet acetone affords adduct **9**, the structure of which was proved by X-ray diffraction analysis. Evidently, this reaction occurs in a solvent cage and starts with protonation of the zwitter-ion **7** by the acid resulting from the hydrolysis of tosyl isocyanate. The contact ion pair **8** thus formed, after evolution of carbon dioxide, is converted into the adduct **9**. In all probability, the latter is formed owing to the occurrence of intermolecular contacts between functional groups. These contacts can be clearly seen in the corresponding X-ray diffraction patterns.[62]

$$Pr^i_3\overset{+}{P}CH_2\overset{-}{C}(CN)COOEt + TsNCO \xrightarrow{H_2O}$$

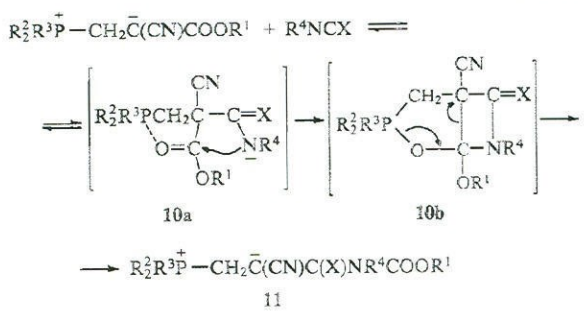


8

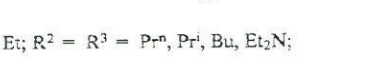
9

The zwitter-ions **7** cause instantaneous polymerisation of ACAs and are readily alkylated with alkyl halides to give the corresponding phosphonium salts.[63] However, their interaction with isocyanates and isothiocyanates follows an unexpected pathway that includes insertion of the iso(thio)cyanate fragment into the C–C bond of the initial zwitter-ion[62,64–66] and leads to zwitter-ions **11** *via* intermediates **10a** and probably **10b** (Scheme 5).

Scheme 5



10a 10b

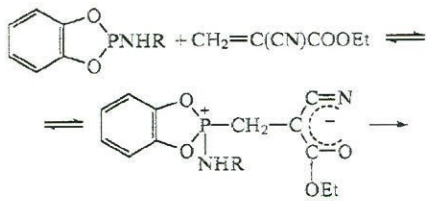


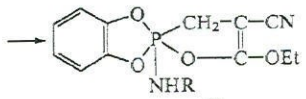
11

R^1 = Me, Et; R^2 = R^3 = Pr^n, Pr^i, Bu, Et_2N;
R^4 = Me, Ph; X = O, S.

The fact that carbanions containing no phosphonium centres react with iso(thio)cyanates without changes in the carbanion skeleton[67] suggests that the rearrangement of the intermediate adduct **10a** formed in the first stage into the thermodynamically more stable zwitter-ion **11** is induced by the phosphonium centre. Apparently, its role consists in intramolecular electrophilic assistance to the attack on the carbonyl carbon atom by the nucleophilic nitrogen atom. In the limiting case, this assistance (which can be regarded as intramolecular electrophilic catalysis) gives rise to the unstable phosphorane **10b** the decomposition of which affords the zwitter-ion **11**. The structures of the reaction products (see Scheme 5) have been confirmed by IR and NMR spectroscopy; for the derivatives of methyl and phenyl isocyanate, X-ray diffraction analysis has also been carried out.[62,65]

The scheme for the insertion of iso(thio)cyanates includes 'opening' of the carbonyl group by the phosphonium centre. This type of reaction is well known for aldehydes and ketones,[68] but it rarely occurs for esters.[69] Therefore, to confirm the above considerations, Gololobov *et al.*[60] have studied the possibility of converting the phosphonium centre in the zwitter-ions **7** into a phosphorane structure through opening of the carbonyl in the alkoxycarbonyl group. This problem was successfully solved when ACAs were made to react with derivatives of trivalent phosphorus with a specific structure.[60] It was found that the formation of spirophosphoranes **12** can be facilitated by both steric and electronic factors. The compounds **12** in which the phosphorus atom in the five-membered ring is bound to a branched alkylamine group are the most stable.

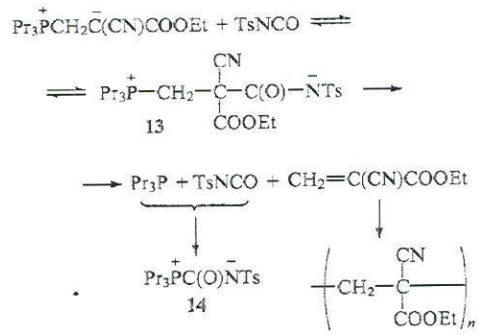




12

R = Bu^t, Hex.

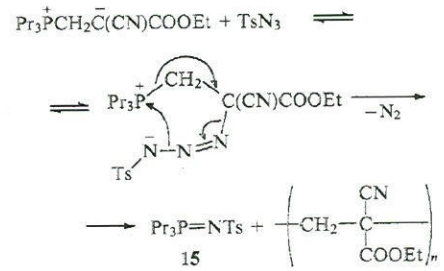
Thus, rearrangement of the adduct **10a** into the zwitter-ion **11** depends on the nucleophilic properties of the negatively charged nitrogen atom. For example, in the case of R^4 = Me or Ph, this atom is nucleophilic enough to attack efficiently the carboxyl carbon atom. However, when toluene-*p*-sulfonyl isocyanate is introduced into the reaction with the zwitter-ion **7**, the nucleophilicity of the nitrogen atom in the resulting adduct is relatively low and, hence, the attack on the carbon atom of the carboxyl group is inefficient. In this case, adduct **13** is stabilised *via* decomposition to give triisopropylphosphine, the initial tosyl isocyanate and the ACA. The latter rapidly polymerises, while triisopropylphosphine reacts with tosyl isocyanate to yield zwitter-ion **14**.[62]



13 14

The structure of the zwitter-ion **14** was proved by X-ray diffraction analysis.[62]

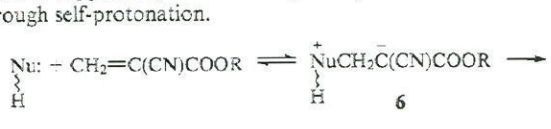
Stabilisation of the adducts arising in the reactions of the zwitter-ion **7** with organic azides is also accompanied by the liberation of an ACA molecule and yields phosphinimines **15**.[62]



15

b. Reactions of 2-cyanoacrylates with nucleophiles containing active hydrogen atoms

When ACAs react with weak nucleophiles, irrespective of the particular experimental procedure, conditions are created under which ACAs instantaneously polymerise. However, when the nucleophile contains an active hydrogen atom, polymerisation of ACA is suppressed, because the primary adduct **6** is stabilised through self-protonation.



6

The interaction of ACAs with thiols of diverse structures under conditions when excess thiol is present (which is achieved by adding the ACA to the reactions mixture) apparently gives rise to zwitter-ion **16** in the first stage of the process. Since the proton at the sulfur atom in this zwitter-ion is relatively active, this species is rapidly self-protonated giving sulfide **17**.[70] Dithio- and thio-acids react with ACAs in a similar way.

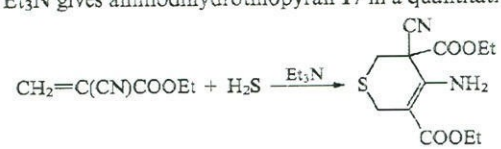
$$RSH + CH_2{=}C(CN)COOEt \rightleftharpoons \underset{H}{RS}\overset{-}{C}H_2\overset{-}{C}(CN)COOEt \longrightarrow RSCH_2CH(CN)COOEt$$

16 **17**

R = Alk, Ar, $HOCH_2CH_2$, $HSCH_2CH_2$, $HCl\cdot NH_2CH_2$, $HCl\cdot NH_2CH_2CH(COOH)$, $HOOCCH_2$, Ac, $(EtO)_2P(S)$, $(EtO)_2P(O)$.

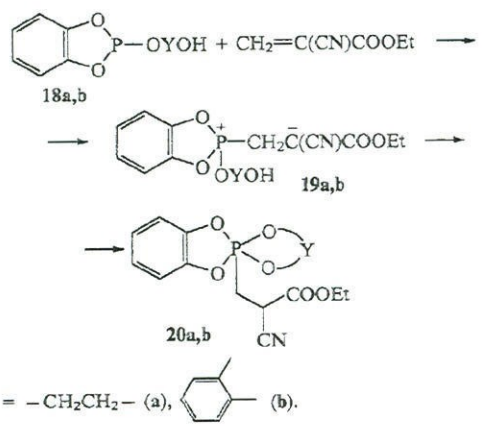
Alcohols can be introduced in this reaction instead of thiols. Normally, alcohols cause only polymerisation of ACAs, because they are less acidic and less nucleophilic than thiols; however, under special conditions (in the presence of an acid the conjugate anion of which is a weak nucleophile), formation of relatively stable adducts of ACAs with alcohols is possible.

Unlike CAA, which reversibly adds water, its esters undergo instantaneous polymerisation in the presence of water. Treatment of ethyl cyanoacrylate with hydrogen sulfide in the presence of 1% of Et_3N gives aminodihydrothiopyran **17** in a quantitative yield.



The interaction of ACAs with phosphites **18a,b** derived from pyrocatechol has been described.[60] The reaction gives rise to cyclic phosphonates **20a,b** *via* the corresponding zwitter-ions **19a,b** (Scheme 6).

Scheme 6



18a,b **19a,b** **20a,b**

Y = $-CH_2CH_2-$ (a), (b).

In these case, too, the zwitter-ions **19a,b** formed initially undergo self-protonation.[60] It should be noted that it is the formation of five-membered phosphorus-containing rings that ensures the success of the synthesis of monomeric products according to Scheme 6. When phosphites that cannot be converted into five-membered phosphoranes like **20** are used in this reaction, oligomeric derivatives are formed.

c. Interaction of 2-cyanoacrylates with weak nucleophiles in the presence of acids

The zwitter-ions **6** formed initially in the reactions of weak nucleophiles with ACAs can also be protonated by an acid present in the reaction mixture and forming no strong bonds with the nucleophile. In this case, the reaction yields salt **21**.

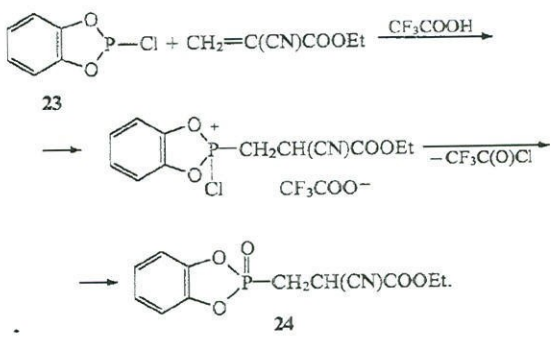
$$Nu: + CH_2{=}C(CN)COOR \rightleftharpoons \underset{\mathbf{6}}{\overset{+}{N}uCH_2\overset{-}{C}(CN)COOR} \xrightarrow{H^+X^-} \underset{X^-}{\overset{+}{N}uCH_2CH(CN)COOR}$$

21

In this reaction, the acid not only protonates the zwitter-ion **6**, but also activates ACA molecules. This has been confirmed by the data of IR spectroscopy,[59] according to which the nitrile and carboxyl groups in ACAs are protonated by acids, and this increases the overall electrophilicity of the ACA molecule.

The activating influence of acids ensures the occurrence of reactions of ACAs with weak nucleophiles, which do not enter into these reactions without acids. Thus 1,3,2-benzodioxachlorophosphole **23** does not react with ACAs in benzene at 20 °C; however, when the reaction mixture contains CF_3COOH, the process yields phosphonate **24** (Scheme 7).[71]

Scheme 7



23 **24**

This reaction is an example of conjugate addition of a weak nucleophile and a strong acid to an ACA; the proton of the acid acts as an inductor. Alcohols and other lowly nucleophilic reagents can also enter into these reactions.[72]

d. Interaction of 2-cyanoacrylates with CH-acids in the presence of bases

In addition to P-, S- and O-nucleophiles, C-nucleophiles (derivatives of CH-acids) can also add to ACAs under certain conditions giving rise to monomeric compounds (Scheme 8).[73]

Scheme 8

$$B: + CH_2{=}C(CN)COOEt \rightleftharpoons \underset{\mathbf{6b}}{\overset{+}{B}CH_2\overset{-}{C}(CN)COOEt} \xrightarrow{1b} \text{Polymer},$$

1b

$$B: + \underset{\mathbf{25}}{CH_2(X)Y} \rightleftharpoons \overset{+}{B}H + \underset{\mathbf{26}}{\overset{-}{C}H(X)Y},$$

$$\overset{-}{C}H(X)Y + CH_2{=}C(CN)COOEt \rightleftharpoons \underset{\mathbf{27a}}{Y(X)CHCH_2\overset{-}{C}(CN)COOEt},$$

$$\mathbf{27a} + \overset{+}{B}H \longrightarrow \underset{\mathbf{27}}{Y(X)CHCH_2CH(CN)COOEt} + B:$$

B: — amine;

X = H, COOR (R = H, Et);

Y = NO_2, CN, Ac.

This version of the Michael reaction is possible only for those CH-acids that react with minor amounts of amines (present as catalysts of the reaction) much more rapidly than ACAs react with these amines. Thus, sufficiently basic amines (B) and relatively strong CH-acids with $pK_a < 13$ (for example, **25**) should be used. The acids should be rapidly converted into the conjugated bases **26**, which would either cause polymerisation of the ACA or react with the ACA to give adduct **27a**. Thus, Scheme 8 reflects a fairly complex system of equilibrium processes, the outcome of which

depends on the acidity of the CH-acid, basicity of amine B, electrophilicity of the ACA, the nature of the solvent, temperature and the order of mixing the reactants.

The results obtained in the study cited[73] showed that the Michael reaction involving ACAs can be used as a general method for the synthesis of esters of substituted cyanocarboxylic acids. The method is suitable for the preparation of various functionally substituted compounds.

V. Prospects for the application of 2-cyanoacrylates

Although the intense development of the 'monomeric' chemistry of ACAs has started not long ago, it has led to two important consequences. On the one hand, the chemistry of ACAs has stimulated investigation of the chemical properties of the zwitterions 7 formed by ACAs and trialkylphosphines, and this has resulted in the discovery of the insertion of the carbamide fragment into the C–C bond (Scheme 5). This, in turn, stimulated the development of a new branch of catalysis, namely, intramolecular electrophilic catalysis by a phosphonium centre. On the other hand, even the first studies on CAA and its esters provided grounds to expect that new ACAs would be synthesised, and this would markedly extend the performance characteristics of cold-setting adhesives and open up new ways for their use in industry, medicine and organic synthesis.

1. The ways to extend the temperature range of performance of adhesives based on 2-cyanoacrylates

The strength of gluing surfaces together with an ACA depends on at least two factors, all other factors being the same, namely, the adhesive capacity of the cyanoacrylate itself and on the stability of the adhesive joint under the conditions of its performance (temperature, moisture content and hostility of the medium).

Industrially manufactured methyl and ethyl 2-cyanoacrylates form high-strength adhesive joints at room temperature; however, the stability of these joints at elevated (> 80–100 °C) or low (< −100 °C) temperatures is relatively low (especially in hostile or moist media). At the same time, ample experimental material on this topic implies that the temperature range of operation of cyanoacrylate adhesives have markedly extended, and their performance characteristics have improved.

The relatively low stability of ACA polymers used under rigorous conditions can be explained by the fact that the polymer backbone contains a quaternary carbon atom (see Scheme 4). Polymers incorporating this fragment are known to possess low thermal stabilities.[74] Therefore, to increase the thermal stability of adhesive joints based on ACAs, the structure of the polymer backbone should be modified by introduction of fragments that would enhance the tolerance of the chain to high temperatures and hostile media (mostly water at various pH). The existing theoretical calculations[4,75,76] provide only general recommendations on the increase in the quality of adhesives based on ACAs.

One of the possible ways of solving this problem is elaboration of cross-linked structures.[77] Two approaches to the formation of 'cross-linked' structures based on ACAs have been considered in the literature. One of them involves introduction of unsaturated carbon–carbon bonds into the ester fragment of ACAs; subsequently, these bonds ensure cross-linking of the structure.

Allyl and propargyl 2-cyanoacrylates as well as other esters of CAA containing more bulky unsaturated groups have low viscosities; this is a necessary condition for attaining the interfacial contact between the adhesive and the substrate at the first stage of the formation of an adhesive joint.[22,46,78–80] Under the action of traces of moisture or other active reagents, the C=C bond of the acrylate is cleaved on the surfaces being glued together.[78,81] Study on the thermodynamics of polymerisation of allyl cyanoacrylate and allyloxyethyl cyanoacrylate[82] makes it possible to conclude that at room temperature these monomers are completely converted into the corresponding polymers by an anionic mechanism, and above 100 °C, cross-linked structures are formed as a result of rupture of the multiple bonds in the allyl and propargyl fragments.[46,78,79,83] It has been noted[84] that the interfacial interaction between substrate and adhesive is due to van der Waals and dipole–dipole forces. In addition to these adhesive forces, chemical bonds of various natures (adsorption theory of adhesion) contribute to the interaction.[85] It is noteworthy that, whereas the C=C bond of the acrylate is cleaved by an anionic mechanism, rupture of multiple bonds in the ester fragment of the molecule occurs only with the participation of free radicals.[78] As a result, an adhesive joint based on unsaturated esters of CAA possesses better performance characteristics than a similar joint based on saturated derivatives.[46,86] The main drawback of cross-linked structures based on unsaturated 2-cyanoacrylates (regarding their practical use) is that in this case, strengthening of adhesive joints occurs only at elevated temperatures (> 100 °C). However, it is often necessary that joints be strengthened below 100 °C. In addition, this procedure can yield a rigid cross-linked polymer and, consequently, the adhesion layer can become brittle.[79] Elastomers can be partly dissolved in ACAs during gluing to give interpenetrating networks[87] (the process is described in terms of the diffusion theory of adhesion). The second approach to the production of a cross-linked adhesive layer is based on copolymerisation of methyl or ethyl cyanoacrylates with unsaturated compounds of various types. Apparently, by selecting an appropriate comonomer, one can obtain adhesive joints with properties varying over a wide range. This approach is more advantageous, because in some cases, a 'cross-linked' adhesive joint can be obtained at low temperatures. Unsaturated compounds containing electronegative polar groups have been used as comonomers, because, on the one hand, owing to these groups, compounds enter in the copolymerisation with ACAs and, on the other hand, these substituents ensure additional cohesion with the substrate. This line of research has led to impressive progress.[3,4,87–95] Evidently, the structure of 2-cyanoacrylates derived from diols[37] and triols[96] is nearly ideal, because in these cases, a cross-linked adhesive joint is formed rapidly under conditions close to those used for the polymerisation of the main monomer. Unfortunately, at present, it is fairly difficult to produce bis- and tris-cyanoacrylates in large amounts. Some methods proposed for their synthesis[34,37] are labour-consuming and expensive; direct esterification of CAA[41–43] or its chloride as well as transesterification of methyl cyanoacrylate with diols[39] can be used only on a laboratory scale.

Judging by several publications,[77,97–103] the research aimed at the involvement of esters of 2-cyano-2,4-pentadienoic acid in the copolymerisation with ACAs is proceeding vigorously. The derivatives of ethylene glycol and 2-cyano-2,4-pentadienoic acid are especially efficient.[7] These esters polymerise at room temperature in the presence of the same catalysts that induce polymerisation of ACA to give a cross-linked structure. It has been shown[77,97] that the performance characteristics of ACAs are markedly improved when they are used as mixtures with butadiene derivatives.

These cross-linking reagents are synthesised by the Knövenagel reaction between the corresponding esters of cyanoacetic acid and aldehydes (Scheme 9).[98,99]

Scheme 9

$$CH_2(CN)COOEt + R'CH{=}CHCHO \xrightarrow[-H_2O]{ZnCl_2} R'CH{=}CHCH{=}C(CN)COOEt$$

R′ = H, Me.

A significant feature of the process shown in Scheme 9 is that anhydrous zinc chloride dissolved in dioxane or THF is used as the catalyst. A method for the synthesis of bis-2-cyanopentadienoates derived from diols containing disiloxane units in the chain has been recently described in a patent.[102]

on them and thus fix any traces left there, for example, fingerprints.[117]

439 (1985)
37. C J Buck *J. Polym. Sci.* **16** 2475 (1978)

2. The use of 2-cyanoacrylates in medicine

The ability of ACAs to polymerise on the surface of a living tissue over periods of several seconds under very mild conditions without special initiation permits these compounds to be regarded as promising surgical materials.[104] It is of prime importance that the polymer based on an ACA is destroyed relatively quickly in a living organism.[105] Polymers based on isobutyl and isoamyl cyanoacrylates are highly biocompatible. It should also be mentioned that ACAs are relatively non-toxic and possess antimicrobial activities. 1,2-Isopropylideneglyceryl cyanoacrylates are quite promising in this respect.[20] Laboratory and clinical tests on the regeneration of tissue cells and restoration of other characteristics of an organism have shown that ACAs ensure strong and elastic connection of tissues; simultaneously, they exhibit antiseptic properties and pose no harmful consequences.[105] Medical adhesives of this type are used during surgical operations on lungs, brains, heart, kidneys, on organs of digestion, sight and respiration, bone tissue and teeth.[3,4,106–109] Efficient medicinal adhesives of the MK series and SO-9m, SO-9t and SO-57 trademarks prepared using fluorinated methacrylates as comonomers have been developed in the former USSR by Russian, Ukrainian and Azerbaijanian chemists. These formulations are non-toxic and tolerant to disinfectants.[110] They possess bacteriostatic and bactericide properties; besides, they are biodegradable in an organism and form no toxic products of decomposition. They also cause no immunological reaction.[111]

The second way of using ACAs in medicine is associated with the development of medical preparations of prolonged action based on them. A procedure has been elaborated for incorporating medical preparations into an ACA-based polymeric matrix. When an ACA is introduced into an intensely stirred solution of a drug, it polymerises to give particles with a size of 170–350 nm containing molecules of the drug sorbed in the polymeric matrix. This procedure was used to obtain immobilised apomorphine[112] and oxytocin.[113] The procedure is general and, apparently, it can be used in several variants.

3. Other applications of 2-cyanoacrylates

Polymers based on ACAs are used to produce photo- and electrono-resists. By chemical deposition of perfluoroethyl cyanoacrylate vapour on a support, a photoresist with a sensitivity of 0.2 J cm^{-1} has been obtained.[114] Positive electronoresists have been obtained using homopolymers of ACAs and their copolymers with functionally substituted monomers.[108] Lengthening of the hydrocarbon chain in the ester group of ACAs markedly decreases the adhesive properties of these compounds. Alkyl cyanoacrylates in which the alkyl chain consists of more than six methylene units have found application in the formation of Langmuir–Blodgett monomolecular layers.[115] Monolayers are formed by polymerisation of CAA esters (from hexyl to decyl ester) directly on the water surface. Since the energy of interaction of the cyano-group in the polymer with water is relatively low (14.6 kJ), the monolayer can be easily transferred on a solid support. At the same time, monomolecular layers of poly(alkyl cyanoacrylates) exhibit some adhesion both to hydrophilic and to hydrophobic surfaces. The above technology for the preparation of Langmuir–Blodgett films can be used in the production of micro-instruments by the submicron technology.

Cyanoacrylates are readily soluble in liquid carbon dioxide;[116] therefore, ACAs packed in aerosol bottles can be used in those cases where a high concentration of ACA vapour is needed. It is clear that the aerosol use of ACAs would help to solve some unexpected problems, because it would permit almost instantaneous production of a polymeric adhesive surface on various objects. ACA vapours deposited on various surfaces polymerise on them and thus fix any traces left there, for example, fingerprints.[117]

* * *

The data presented in this review provide grounds for believing that at present, a new stage in the development of the chemistry of ACAs has started. This can lead to development of cold-setting adhesives with better performance properties; in addition, new applications of CAA derivatives can appear, and the use of ACAs in organic and organometallic synthesis can become wider.

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