Organic Chemistry

Synthesis of functionally substituted 2-cyanoacrylates

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The conditions for the Knoevenagel synthesis of 2-cyanoacrylates containing double and triple bonds in the alkoxycarbonyl group have been studied. It was found that the esters are formed in 10—70 % yields by the condensation of the respective cyanoacetates with formaldehyde in the 1 : 1 ratio in the presence of piperidine, followed by the pyrolysis of the oligomers formed *in vacuo* at 170—200 °C in the presence of *para*-toluenesulfonic acid. The compounds synthesized readily undergo polymerization at room temperature and can be used as the basis for thermostable rapidly polymerizing adhesives.

Key words: cyanoacetates, 2-cyanoacrylates, paraform, formaldehyde, 2-cyanoacrylates.

2-Cyanoacrylates (CA) serve as the base for adhesives, quickly polymerizing at room temperature.[1] Of these compounds, the alkyl esters are used most widely.[2] The use of alkoxyalkyl 2-cyanoacrylates for this purpose has been reported.[3] The low thermal stability of cyanacrylate adhesives based on esters of this type is their main disadvantage. A possible way to increase the thermal stability of cyanacrylate adhesives is the use of CA containing multiple bonds in the alkoxycarbonyl group as the base for these adhesives.

The present work deals with the synthesis of CA (**1**—**10**) containing a double or triple bond in an alkyl or alkoxyalkyl group by the traditional method based on the Knoevenagel reaction[4] of cyanoacetates with formaldehyde in the presence of a catalyst followed by the pyrolysis of the oligomeric condensation product *in vacuo* at a high temperature.

The high temperature of the pyrolysis complicates the synthesis of the highly reactive compounds **1**—**10**. Therefore, it was important to find the conditions for the condensation of cyanoacetates with formaldehyde resulting in oligomers with a minimum molecular mass, so that the latter would undergo pyrolysis at 200—220 °C. At higher temperatures, the oligomers containing allyl moieties in the chain are transformed into a nonmelting and insoluble state due to cross-linking, which results in a drastic decrease in the yield of the target product. Moreover, the probability of transformations of oligomers and monomers involving the CN-group (*e.g.*, cyclization or cross-linking of monomers) under these conditions increases, which also impairs the quality of the target product and significantly decreases its yield.

A study of the effect of the solvent, catalyst, and the

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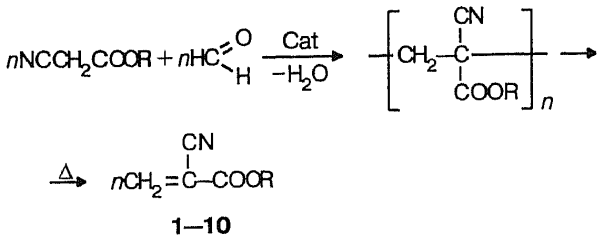
Scheme 1



1—10

R = : $CH_2CH=CH_2$ (**1**); $CH_2CH_2OCH_2CH=CH_2$ (**2**);
$CH_2CH_2CH_2OCH_2CH=CH_2$ (**3**);
$CH_2CH(CH_3)OCH_2CH=CH_2$ (**4**);
$CH_2CH_2CH_2CH_2OCH_2CH=CH_2$ (**5**);
$CH_2CH_2OCH_2CH_2OCH_2CH=CH_2$ (**6**);
$CH_2COOCH_2CH=CH_2$ (**7**); $CH_2C{\equiv}CH$ (**8**);
$CH_2CH_2OCH_2C{\equiv}CH$ (**9**); $CH(CH_3)CCl=CCl_2$ (**10**).

Cat - catalyst.

ratio of the starting materials on the yield and purity of the CA showed that the most convenient solvent is isopropanol and the best source of formaldehyde is 36—40 % paraform. The hemiacetal resulting from the reaction of formaldehyde with isopropanol[5] undergoes condensation more quickly than formaldehyde generated from paraform in a heterogeneous medium, *e.g.*, in benzene (Fig. 1).

To obtain a high-purity CA with good adhesive properties, an equimolar ratio of the starting materials provides the optimum conditions (Table 1).

It is known that the condensation of cyanoacetates with formaldehyde is effectively catalyzed by bases,[6] *e.g.*, diethylamine and piperidine. The choice of the

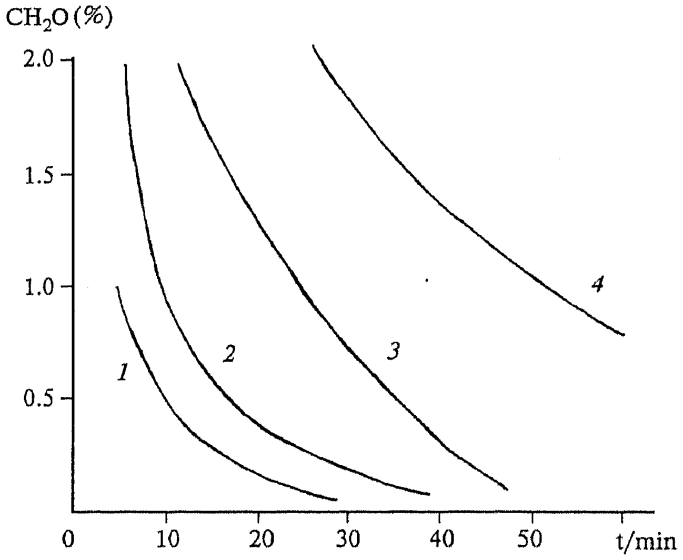
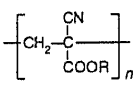


Fig. 1. Effect of the time of condensation of allyl cyanoacetate (1 mol) with formaldehyde (1 mol) in isopropanol (curves *1*, *2*) and in benzene (curves *3*, *4*) in the presence of 0.002 mol piperidine (curves *1*, *3*) or 0.005 mol diethylamine (curves *2*,*4*) on the content of free formaldehyde in the reaction mixture.

Table 1. Effect of the ratio of the starting reagents on the yield, purity, and adhesive strength of compound **1**

Cyanoacetate : formaldehyde ratio	Yield of **1** (%)	The content of the main compound (%)	Shear strength /MPa
1.05 : 1	62	97.5	8.0
1 : 1	70	99.9	11.0
1 : 1.05	65	98.8	6.0

Table 2. Molecular masses and temperatures of pyrolysis of the oligomers



Monomer	R	$\overline{M}^a$		$\overline{M}_w/\overline{M}_n$	T_p/°C[b] (1 Torr)
		$\overline{M}_w$	$\overline{M}_p$		
1	$CH_2CH=CH_2$	620	310	2.00	170—190
3	$(CH_2)_3OCH_2CH=CH_2$	825	383	2.15	200—220
4	$CH_2CH(CH_3)OCH_2CH=CH_2$	694	483	1.44	190—210
7	$CH_2COOCH_2CH=CH_2$	732	530	1.38	200—220

[a] $\overline{M}$ — is the mean molecular mass.
[b] T_p — is the pyrolysis temperature.

catalyst dependes on several parameters (duration of the reaction, the temperature of oligomer pyrolysis, the yield of the monomer, its purity and adhesive properties). The reaction was considered to be completed when the amount of free formaldehyde in a reaction mixture was below 0.1 %.

It was found that the rate of condensation of cyanoacetates with formaldehyde in the presence of piperidine is higher than in the case of diethylamine, and that high conversion and good yields of the target products are achieved in this case.

It was previously assumed[7] that the formation of oligomers during the condensation of cyanoacetates with formaldehyde under homogeneous conditions in the presence of basic catalysts occurs by anionic polymerization of the CA formed. Evidently, compounds **1—10** behave similarly. According to several authors,[8] water liberated during condensation can catalyze the polymerization. As a result, oligomers with terminal hydroxyl groups are formed.

Depending on the type of terminal groups of the oligomers, their pyrolysis can give water and piperidine along with a monomer. The water was absorbed by phosphoric anhydride or polyphosphoric acid. Piperidine, which is the most dangerous admixture with respect to the yield and purity of the target product, was neutralized with *para*-toluenesulfonic acid, which is also an inhibitor of anionic polymerization of the monomer formed.

As estimated by gel permeation chromatography, the oligomers obtained under the optimum conditions in the presence of piperidine have medium molecular masses (Table 2). The oligomers having a branched group (the oligomer derived from monomer **4**) or an allyoxycarbonyl

group (the oligomer of monomer **7**) in the side chain have lower polydispersion than the oligomers with an unsubstituted linear group (oligomers of monomers **4** or **3**). In this case, the molecular mass is greatly affected by CA dimers. The pyrolysis of oligomers having low molecular masses occurs with a high rate at temperatures which are rather low for compounds of this type.

The pyrolysis of oligomers having long ether fragments resulted in an increased amount of volatile products, which in the end decreases the yields of the respective monomers significantly (see Table 3).

All of the CA synthesized undergo polymerization between the surfaces of the materials to be glued together. They display adhesive properties toward ferrous and nonferrous metals, glass, wood, ceramics, plastics, *etc.*, but not toward polyolefins and fluoroplastics.

The composition and structure of the CA were confirmed by elemental analysis and IR and ^{1}H NMR spectral data (Table 3).

The IR spectra of the CA contain characteristic absorption bands (ν/cm^{-1}): 1620—1640 (acrylate C=C) and 1640—1660 (allylic C=C) for compounds **1**—**7**; 1720—1760 (C=O), 2250—2260 (C≡N); 2100 and 3300 (C≡C) for compounds **8** and **9**; 800 (C—Cl) for compound **10**.

All of the CA synthesized are liquid compounds. They were purified by fractionation *in vacuo* until the content of the main compound was at least 99.8 %. The

Table 3. Yields and parameters of 2-cyanoacrylates

Compound	Yield (%)	B.p./°C (*p*/Torr)	n_D^{20}	Molecular formula	Calculated (%) / Found			^{1}H NMR ((CD$_3$)$_2$CO) δ (*J*/Hz)
					C	H	N	
1	70	78(1)	1.4610	$C_7H_7NO_2$	61.31 61.42	5.11 5.09	10.22 10.08	4.74 (m, 2 H, C<u>H</u>$_2$CH=)
2	60	107(1)	1.4620	$C_9H_{11}NO_3$	59.67 59.26	6.08 6.08	7.73 7.87	3.68 (m, 2 H, C<u>H</u>$_2$OCH$_2$CH=CH$_2$) 4.00 (m, 2 H, C<u>H</u>$_2$CH=) 4.40 (m, 2 H, OC<u>H</u>$_2$CH$_2$)
3	55	101(1)	1.4622	$C_{10}H_{13}NO_3$	61.54 61.19	6.67 6.75	7.18 7.19	2.00 (m, 2 H, CH$_2$C<u>H</u>$_2$CH$_2$) 3.56 (t, 2 H, C<u>H</u>$_2$OCH$_2$CH=CH$_2$) 3.95 (m, 2 H, C<u>H</u>$_2$CH=) 4.40 (t, 2 H, OC<u>H</u>$_2$CH$_2$CH$_2$)
4	40	116(4)	1.4570	$C_{10}H_{13}NO_3$	61.54 60.82	6.67 6.62	7.18 7.18	1.30 (d, 3 H, CH$_3$) 3.50 (d, 2 H, OC<u>H</u>$_2$CH(CH$_3$)) 4.00 (m, 2 H, C<u>H</u>$_2$CH=) 5.08 (m, 1 H, CH$_2$C<u>H</u>(CH$_3$))
5	20	126(1)	1.4640	$C_{11}H_{15}NO_3$	63.16 62.81	7.18 7.55	6.70 6.47	1.74 (m, 4 H, CH$_2$C<u>H</u>$_2$CH$_2$CH$_2$) 3.45 (d, 2 H, C<u>H</u>$_2$OCH$_2$CH=CH$_2$) 3.94 (m, 2 H, C<u>H</u>$_2$CH=) 4.18 (m, 2 H, OC<u>H</u>$_2$CH$_2$)
6	10	130(0.5)	1.4670	$C_{11}H_{15}NO_4$	58.67 58.01	6.67 6.81	6.22 6.92	3.62 (m, 4 H, C<u>H</u>$_2$OC<u>H</u>$_2$) 3.81 (m, 2 H, C<u>H</u>$_2$OCH$_2$CH=CH$_2$) 4.00 (m, 2 H, C<u>H</u>$_2$CH=) 4.45 (m, 2 H, COOC<u>H</u>$_2$)
7	25	114(0.5)	1.4633	$C_9H_9NO_4$	55.38 54.95	4.60 4.73	7.18 7.78	4.68 (m, 2 H, CH$_2$CH=) 4.82 (c, 2 H, CH$_2$COO)
8	50	M.p. 34	–	$C_7H_5NO_2$	62.22 61.91	3.73 4.02	10.37 10.37	2.42 (t, 1 H, CH) 4.18 (d, 2 H, CH$_2$)
9	20	115(1)	1.4730	$C_9H_9NO_3$	60.34 60.21	5.03 5.22	7.82 7.83	2.96 (t, 1 H, CH) 3.85 (m, 2 H, C<u>H</u>$_2$OCH$_2$C≡) 4.25 (d, *J* = 4,1, 2H, CH$_2$C≡) 4.47(m, 2 H, OC<u>H</u>$_2$CH$_2$)
10	25	120(2)	1.5100	$C_8H_6NO_2Cl_3$	32.72 32.79	2.35 2.40	5.50 5.39	1.30; 1.40 (d, *J* = 6, 3 H, CH$_3$) 4.73 (q, *J* = 6, 1 H, CH) 5.33; 5.63 (d, 2 H, CH$_2$=C)

Note. The ^{1}H NMR spectra of compounds **1**—**7** contain signals of the allyl group protons: 5.15—5.43 (m, 2 H, CH$_2$=) and 5.86—6.00 (m, 1 H, CH); the spectra of compounds **1**—**9** contain signals of the CH$_2$=C(CN) group protons: 6.0; 7.1 (d, 2 H). Found for compound **10** (%): Cl 41.84; calculated (%): Cl 42.00.

CA are stable when stored in a light-protected place at a temperature near +5 °C.

Thus, the optimum conditions for the synthesis of CA with unsaturated alkoxycarbonyl groups, which can undergo cross-linking at elevated temperatures and can be used as the base for thermostable rapidly polymerizing adhesives,[9,10] have been found.

Experimental

^{1}H NMR spectra of 10 % solutions were recorded in $(CD_3)_2CO$ on a Bruker WP-200 SY spectrometer.

IR spectra were obtained in KBr pellets on a UR-20 spectrophotometer.

The purity of the CA was determined by GLC on a Khrom-5D chromatograph with a catharometer detector, 2 m stainless steel columns (5 mm diameter), the 10% XE-60 phase on Chromaton N-AW, helium as the carrier gas (rate $0.5 \cdot 10^{-6}$ m^3 s^{-1}). Samples were introduced as 10 % solutions in methylene dichloride.

The molecular masses were determined on a Millikhrom liquid chromatograph with a UV detector, λ 280 nm. The sorbent elaborated in the Institute of Organoelement Compounds of the RAS consisted of microspheres of a styrene—divinylbenzene copolymer.[11] The column was 175×2.8 mm; THF was used as the eluent. The feed rate of the eluent was 50 μL min^{-1}. The calibrating plot of the logarithm of the molecular mass *vs.* the eluted volume was constructed using polystyrene standards.

Cyanoacetates were obtained by the procedure in Ref. 12 and distilled *in vacuo* with hydroquinone in a stream of helium.

The solution of paraform (40 g) in isopropanol (60 g) was prepared by boiling with stirring. The solution was cooled, filtered, and analyzed by the sulfite method.[13]

Allyl 2-cyanoacrylate (1). A 40 % solution of formaldehyde in *i*-PrOH (75g; 1 mol CH_2O) and piperidine (0.2 mL, 0.172 g) was placed in a four-necked flask equipped with a stirrer, a dropping funnel, a reflux condenser, and a thermometer. The mixture was heated to 60 °C, and allyl cyanoacetate (125 g, 1 mol) was added dropwise with constant stirring. The content of the unreacted formaldehyde in the reaction mixture was determined after 10, 20, and 30 min. When the concentration of free formaldehyde was less than 0.1 %, an isopropanol—water azeotropic mixture was distilled off, benzene (300 mL) was added, and the remaining water was distilled off as a benzene—isopropanol—water ternary azeotropic mixture. Then P_2O_5 (6 g), hydroquinone (3 g), and *para*-toluenesulfonic acid were added to the reaction mixture, and pyrolysis was performed *in vacuo* at 170—190 °C. The crude monomer obtained was fractionated *in vacuo*.

Monomers **2—10** were synthesized in a similar way. The properties of compounds **1—10** are given in Table 3.

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