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Preparation and Reactions of Chloro-derivatives of Nitriles

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Published information on the synthesis and reactivity of chloro-derivatives of nitriles is summarised, and methods are examined for the preparation of such derivatives of acetonitrile, acrylonitrile, methacrylonitrile, crotononitrile, and benzonitrile. Research on the mechanism of reactions undergone by the derivatives is reported. A list of 113 references is included.

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I. INTRODUCTION

The use of nitriles, in particular acrylonitrile, in aeronautics, motorcar manufacture, building, light industry, and agriculture, as well as exploitation of the high calorific value of several nitriles in special fuels, explains the continuously increasing production of several nitriles.

The presence of a chlorine atom in nitriles increases the synthetic and practical possibilities of this class of compounds. Chloro-derivatives of nitriles are of both theoretical and practical interest, and have therefore attracted the attention of research workers. Such compounds are intermediates in various organic synthesis, while unsaturated chlorinated nitriles find application in the production of polymers having interesting properties.

The little information available on the synthesis of chlorinated nitriles has appeared mainly in the patent literature. Only two books have been published on fundamental aspects of the reactivity of nitriles[1,2]. No systematic results are available on the preparation and reactivity of the halogeno-derivatives. Since 1960 papers have appeared on the synthesis of chloro-derivatives of nitriles, and during the past 5-7 years several investigations of the reactivity of chloroacrylonitriles have been published. The present Review summarises results for the preparation of chloro-derivatives of nitriles and investigations of their reactions.

II. PREPARATION OF CHLORO-DERIVATIVES OF NITRILES

Direct chlorination is one of the main methods for obtaining chloro-derivatives of nitriles. The earliest papers on this process appeared during the nineteenth century[3-5]. Acetonitrile is readily chlorinated to give a high yield of trichloroacetonitrile:

$$CH_3CN + 3Cl_2 \rightarrow Cl_3CCN + 3HCl\ .$$

Chlorination can be initiated photochemically with natural or artificial radiation (at 50-80°C), catalysed by platinum or silver chloride on asbestos, or effected by a combination of these treatments[6,7,9]. The reaction is also accelerated by preliminary saturation of the acetonitrile with hydrogen chloride.

Publications on liquid-phase chlorination reflect no generally accepted view on why interruption of the process does not prevent the formation of completely chlorinated products. Analysis of the reaction mixture shows the absence of mono- and di-chlorinated derivatives of acetonitrile. Stepanov and Shirokova[8] explain such discrepancies on the assumption that the rate of chlorination of the starting material is considerably lower than those of the partly chlorinated products. In the Reviewer's opinion such a hypothesis is implausible as it is devoid of analgies. Carboxylic acids and their derivatives can readily be chlorinated in stages, which applies also to many other compounds containing activated methyl and methylene groups. A more plausible hypothesis is that hydrogen chloride liberated on chlorination adds to the partly chlorinated nitrile, and the resulting nitrilium salt or tautomeric imidoyl chloride is chlorinated considerably more rapidly than is the initial nitrile:

$$CH_3CN + Cl_2 \xrightarrow{\text{slow}} (ClCH_2{-}C{\equiv}NH)^+Cl^-$$
$$(CH_2Cl{-}C{\equiv}NH)^+Cl^- + Cl_2 \xrightarrow{\text{rapid}} (CHCl_2{-}CNH)^+Cl^- + HCl$$
$$(CHCl_2{-}CNH)^+Cl^- + Cl_2 \xrightarrow{\text{rapid}} (CCl_3{-}CNH)^+Cl + HCl$$
$$(CCl_3{-}CNH)^+Cl^- \rightarrow CCl_3{-}CN + HCl.$$

On this hypothesis it was deduced[9] that preliminary treatment of the nitrile with hydrogen chloride should increase its rate of chlorination, which was fully confirmed by experiment.

A process suggested[10] for the continuous catalytic production of chloroacetonitrile CH_2ClCN consists in the gaseous chlorination of acetonitrile. The latter is treated with chlorine diluted with an inert gas at temperatures from 50°C to the boiling point of acetonitrile, with simultaneous exposure of the mixture to light from a mercury lamp or ionising rays[11]. Acetonitrile vapour and chlorine can also be passed through a turbulent-flow reaction vessel[12].

Several publications have appeared on the preparation of chloro-derivatives of acrylonitrile. Methods are based either on direct chlorination or on the dehydrochlorination of $\alpha\beta$-dichloropropionitrile[13,14]. Table 1 lists conditions for the chlorination of acrylonitrile[15-32]. The action of a hydrohalic acid on propiolonitrile in the presence of a copper salt has been claimed[18] to give a 75% yield of a β-halogeno-derivative of acrylonitrile. Processes have been reported for obtaining α-halogenoacrylonitriles[19] by the dehalogenation of $\alpha\alpha\beta$-trihalogenopropionitriles by treatment with a trialkyl or a triaryl phosphite:

$$XCH_2CX_2CN + (RO)_3P \rightarrow CH_2{=}CXCN + (RO_2)POX + RX$$
$$(X{=}Cl,\ Br,\ I)\ .$$

A 91% yield of $\alpha\alpha\beta$-trichloropropionitrile has been claimed[21] when a hydrogen halide is introduced into the chlorination of acrylonitrile. The action of chlorine on

propiolonitrile in an alcoholic or aqueous–alchoholic solution of a copper(II) halide at 30–60°C is stated[22] to give di- and tri-halogenated derivatives of acrylonitrile. Another method has been suggested[23] for obtaining $\alpha\alpha\beta$-trichloropropionitrile, which is very effective in suppressing the growth of weeds among broad-leaved plant crops (Table 1).

Table 1. Conditions of chlorination of acrylonitrile (ACN).

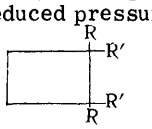
Starting materials	Temp., °C	Catalyst	Contact for	Yield, wt.%			Ref.
				α-ClACN	β-ClACN *cis* + *trans*	α,α,β-tri-chloro-propionitrile	
ACN + Cl_2	200—550	activated carbon	—	68	—	—	15
ACN + Cl_2 (1–3:1)	450—850	—	0.001–1 s	90	—	—	16
ACN + Cl_2	100—600	chlorides or oxides of Cu, Cr, Ni, Mn, Mg, Al, Fe, Ca, Pd, V	—	90	—	—	17
α-Acetoxy-β-chloropropio-nitrile (pyrolysis)	535	—	—	28	35	35	26
ACN + Cl_2	50—70	CCl_4, $CHCl_3$ soln.	—	—	—	95	23
αβ-Dichloropro-pionitrile (pyrolysis)	60 (12 mm)		0.7 s	93	—	—	29
αα-Dichloropro-pionitrile + NH_3	0—15	—	0.5–1 h	64	—	—	31
ACN + O_2 + HCl	150—160 (0.1–10 atm)	—	1–30 s	32.6	—	—	32

A paper on the synthesis and polymerisation of several α-substituted acrylonitriles has reported[25] preparations of α-bromoacrylonitrile, α-chloroacrylonitrile, methylenemalononitrile, methacrylonitrile, and other alkylated acrylonitriles. Isomeric mixtures of *cis*- and *trans*-β- and -α-chloroacrylonitriles can be obtained[26] by the pyrolysis of α-acetoxy-β-chloropropionitrile. Chlorination of acrylonitrile in dimethylformamide will give an approximately 90% yield of αβ-dichloropropionitrile[27]:

$$CH_2{=}CH{-}CN + Cl_2 \xrightarrow{DMF} CH_2Cl{-}CHCl{-}CN .$$

An interesting study[28] of the influence of gaseous hydrogen chloride on the chlorination of acrylonitrile showed that, depending on the concentration of the gas evolved, either a mixture of β-mono- and ααβ-tri-chloropropionitriles or αβ-dichloropropionitrile is formed. If chlorination is continued after the solution has become saturated with hydrogen chloride, the mixture is formed; continued chlorination of this mixture yields only ααβ-trichloropropionitrile. If the reaction is terminated before the solution begins to be saturated with hydrogen chloride, the main product is αβ-dichloropropionitrile.

Nitriles of α-halogenoacrylic compounds can be obtained by the pyrolysis under reduced pressure of compounds of general formula



where R = Cl and R′ = CN.[29] Clorination of acrylonitrile with a mixture of carbon monoxide and chlorine yields αβ-dichloropropionitrile[30]:

$$CH_2{=}CH{-}CN \xrightarrow{CO+Cl_2} CH_2Cl{-}CHCl{-}CN ,$$

The patent literature[31,32] gives several methods for obtaining α-chloroacrylonitrile (Table 1).

The first publications on the preparation of chloro-derivatives of methacrylonitrile appeared around 1950.[34,35] A proposed method was to chlorinate αβ-unsaturated nitriles at high temperatures (up to 600°C). A mixture of βω-dichloromethacrylonitrile with a 61% yield of ω-chloromethacrylonitrile was obtained:

$$CH_2{=}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{-}CN + Cl_2 \xrightarrow{585-600^\circ C} \underset{8\%}{CHCl{=}\overset{\displaystyle CH_2Cl}{\overset{|}{C}}{-}CN} + \underset{61\%}{CH_2{=}\overset{\displaystyle CH_2Cl}{\overset{|}{C}}{-}CN} + HCl .$$

Kondratenko and Khaskin[36] have obtained isomeric chlorohydroxyisobutyronitriles by reaction between methacrylonitrile and chlorine in an aqueous medium. Nitriles of 2-chlorocyclobutanecarboxylic acids have been claimed[37] as products of the cycloaddition of vinyl chloride to acrylonitrile. ω-Chloromethacrylonitrile can be obtained[38] by the action of anhydrous liquid ammonia on αβ-dichloro-α-methylpropionitrile. Lower (C_{3-7}) ω-chloro-nitriles result[39] from the telomerisation of cyanogen chloride and ethylene in the presence of azoisobutyronitrile or di-t-butyl peroxide under 52.5–70 atm.

The few publications that have appeared on halogeno-derivatives of the isomeric crotononitrile relate mainly to the formation of γ-chlorobutyronitrile, αβ-dichlorobutyronitrile, and a small quantity of α-chlorocrotononitrile. Table 2 gives several methods for obtaining chloro-derivatives of crotononitrile under various conditions[40–46].

Table 2. Conditions of treatment of crotonitrile with chlorine.

Temp., °C	Catalyst	Yield of chloro-derivative, wt.%		Ref.
		β-mono	αβ-di	
20—250	—	55—61	—	40—42, 44
595—700	—	57,7	—	43
400—600	—	62	—	45
680	metal oxides	—	91	46

Halogeno-derivatives of aromatic nitriles are used for the synthesis of dyes distinguished by excellent fastness, as well as herbicides, insecticides, etc. The very few publications on the preparation of halogenobenzonitriles relate mainly to the *o*-chloro-derivative, which is the principal starting material for the production of azo-dyes, e.g. Basic Bordeaux, Disperse Violet, etc. Several methods are known for obtaining halogenobenzonitriles by the oxidative ammonolysis of halogenated aromatic hydrocarbons. Application of this process to *p*-chlorotoluene on a catalyst comprising arsenic and vanadium oxides promoted with alkali metals at 250–300°C gives a 66.5% yield of *p*-chlorobenzonitrile[47]. A catalyst comprising vanadium(V) and

iron(III) oxides on alumina can also be used[48]. Table 3 lists conditions for the oxidative ammonolysis of chlorotoluene[49–52].

Table 3. Conditions of formation of chlorobenzonitriles*.

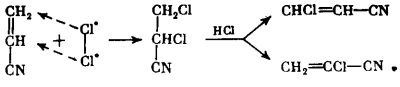
Starting materials	Temp., °C	Catalyst	Yields of isomers, wt.%			Ref.
			ortho	*meta*	*para*	
o-, *m*-, *p*-$ClC_6H_4CH_3$ + O_2 + NH_3 + H_2O*	455	V, Ti, Sn oxides	—	50–80	47	49
p-ClC_6H_4CN + Cl_2	350	V, Sb, Bi, Al oxides	18	49.5	32.5	51
p-ClC_6H_4CN + Cl_2	450	V, Sb, Bi, Al oxides	25	45	30	52

* Proportions of starting materials $ClC_6H_4CH_3 : O_2 : NH_3 : H_2O = 1 : 83 : 19 : 105$.

However, the technical complexity of the suggested methods and the need for expensive catalysts led to the proposal that interesting monomers should be obtained by a single-stage method[53–55] of chlorination of nitriles. A technical scheme has been put forward[57] for the chlorination of C_{2-4} nitriles, in which the reaction vessel contains a stationary layer of catalyst. Since the type of catalyst (perlite, quartz, AG-3 activated carbon) had no clear effect on the yield of products[56], and perlite is inexpensive and readily available, subsequent investigations were made on this catalyst. The highest yields of chloro-nitriles have been observed[57–61] with a molecular ratio of nitrile to chlorine of 2 : 1. With a short period of contact, however, dichloro-derivatives are formed: i.e. chlorine is added. As the time of contact lengthens, α- and β-chloro-nitriles are formed; the maximum yield (80–85 wt.%) is achieved with a time of contact of 5–6 s. Chlorination thus follows an anomalous course, as a consequence of dehydrochlorination of $\alpha\beta$-dichloropropionitrile: i.e. substitutive chlorination takes place. The influence of temperature on the yield of chloro-nitriles is similar to that of the time of contact: at low temperatures dichloro-derivatives are formed, but with rise in temperature their yield diminishes, and that of monochloro-nitriles increases in proportion. Experiments and calculations[62,64] have made it possible to establish optimum conditions for obtaining chloroacetonitrile, α-chloroacrylonitrile, and ω-chloromethacrylonitrile.

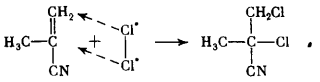
The kinetic and other studies of the chlorination of acrylonitrile and methacrylonitrile have led to a tentative reaction mechanism[57,63,64] in which these nitriles are regarded to a first approximation as unsaturated hydrocarbons[65]. The unusual course of chlorination of the latter was first observed during the nineteenth century[66–69]. Tishchenko[70–74] later found that anomalous chlorination of unsaturated hydrocarbons is observed when a quaternary carbon atom is adjacent to the double bond; the main product is then an isomeric monochloride in which the double bond has been displaced, accompanied by only a small quantity of the dichloride.

On the basis of the mechanism of the anomalous chlorination of hydrocarbons it has been suggested[57–64] that the chlorination of acrylonitrile can be represented by the scheme

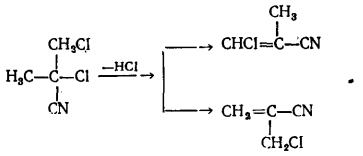


Chlorine adds to the acrylonitrile molecule, the double bond opens, and $\alpha\beta$-dichloropropionitrile is formed. At high temperatures this is accompanied by dehydrochlorination of the dichloro-derivative to give α- and β-chloroacrylonitriles. This scheme is supported by experiment, since at sufficiently high temperatures (350–380°C) with contact lasting for 6–7 s the competitive addition of both chlorine atoms to acrylonitrile diminishes, and a monochloro-nitrile is formed.

The chlorination of methacrylonitrile can probably be represented

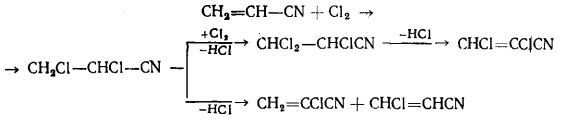


However, the product is unstable, and stabilisation occurs by elimination of hydrogen chloride to form ω-chloromethacrylonitrile:

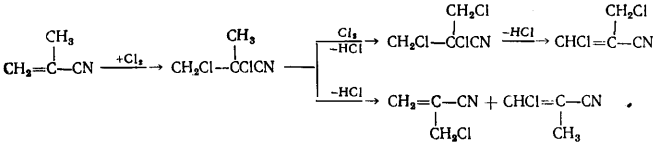


The direction of the dynamic effect is opposite to that of the static effect of conjugation. Therefore methacrylonitrile undergoes chlorination under more severe conditions than does acrylonitrile.

On the basis of the above investigations and the classical interpretation of the anomalous chlorination of unsaturated hydrocarbons it has been suggested[57,64] that the chlorination of acrylonitrile can be represented by the scheme

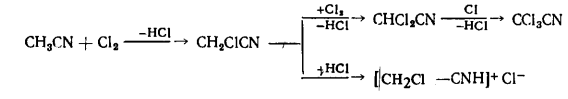


and that of methacrylonitrile by



Adequate attention has been paid to aspects of the liquid-phase chlorination of acetonitrile[33,75,76]. Chlorination involves intermediate formation of a nitrilium salt to give finally trichloroacetonitrile.

The vapour-phase chlorination of acetonitrile with a molecular ratio nitrile : chlorine = 2 : 1 at 350°C for 5–6 s gives mainly chloroacetonitrile with a small quantity of trichloroacetonitrile[57,58,100]. Two fractions corresponding to these products were isolated. Hardly any dichloroacetonitrile was observed. Traces of a nitrilium salt are also formed[100]. The salt decomposes at high temperatures, so that it cannot be formed in vapour-phase chlorination at 350–360°C. The nitrilium salt is most probably formed on cooling, when chloroacetonitrile reacts with hydrogen chloride. From the above considerations the mechanism



has been suggested for the chlorination of acetonitrile.

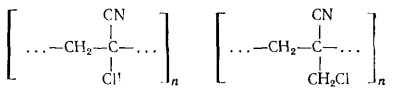
It has thus been ascertained that the vapour-phase chlorination of nitriles follows the anomalous chlorination mechanism of unsaturated hydrocarbons. This method can be used also to obtain unsaturated monochloro-derivatives of other classes of compounds.

III. REACTIONS AND PRACTICAL APPLICATION

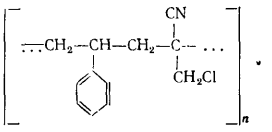
Chloro-derivatives of nitriles find application as insecticides. They also exhibit bactericidal properties[24], and are very effective against soil pests[109].

Chloro-derivatives of nitriles are a little investigated class of compounds. Few papers have appeared on the reactions of the unsaturated representatives, since hitherto they have been unavailable. Development of methods for the preparation of chloro-derivatives of aliphatic and aromatic nitriles has made it possible to study their reactions. A process has been claimed[20] for obtaining derivatives of α-chloro-β-p-hydroxyphenylpropionitrile, which can be used as intermediates in the production of medicinals.

Polymeric materials obtained from chlorine-containing monomers possess valuable properties, in particular fire resistance. The presence of a nitrile group together with a chlorine atom in a monomer may confer on the polymers also frost resistance, gas impermeability, and resistance to corrosive media. It is therefore of practical interest to study the polymerisation of chloroacrylonitrile and chloromethacrylonitrile as examples of such monomers. α-Chloroacrylonitrile has been used[77-81] to obtain polyconjugated polymers both of linear (polyvinylene) structure and of ladder structure with fused naphthyridine rings. As well as the synthesis of homopolymers



the possibility has been investigated of the copolymerisation of chloromethacrylonitrile with styrene to give



Chloroacrylamides have been obtained[82] by conversion of the nitriles into amides under conditions of acid hydration:

$$CH_2{=}CCl{-}CN \xrightarrow{HOH} CH_2{=}CCl{-}C\!\!<\!\!\begin{matrix}NH_2\\ O\end{matrix}$$

Chloro-derivatives of nitriles are interesting starting materials for the single-stage preparation of chloro-derivatives of unsaturated acids by hydration in the presence of 75% sulphuric acid. Such acids can be formed also[82-85,105] by direct chlorination of acrylic and methacrylic acids:

$$CH_2{=}CCl{-}CN \xrightarrow{HOH} CH_2{=}CCl{-}COOH \xleftarrow[150-170^\circ]{Cl_2} CH_2{=}CH{-}COOH .$$

Addition of alcohols to α-chloroacrylonitrile in the presence of AV-17 anion-exchange resin, sodium methoxide, and amines is catalysed by the amines themselves[86-89]:

$$ROH + CH_2{=}CCl{-}CN \rightarrow ROCH_2CHCl{-}CN$$

R=CH_3, $CH_2{-}CH{=}CH_2$, $CH_2C{\equiv}CH$

$$R_2NH + CH_2{=}CCl{-}CN \rightarrow R_2NCH_2CHCl{-}CN$$

R′=R=C_3H_7; R=R′=CH_3; R=R′=C_2H_5; R=R′=C_4H_9 .

Nucleophilic substitution by treatment with alcohols has been used to examine the reactivity of the chlorine in chloro-nitriles and to develop a procedure for obtaining hydroxy-derivatives of aliphatic nitriles[90,91]. The reactions of C_1–$_7$ aliphatic alcohols and of cyclic and unsaturated alcohols have been studied[110]:

$$ClCH_2CN + ROH \xrightarrow{NaOH} NCCH_2OR + NaCl + HOH$$

R=CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15},



, $CH_2{-}CH{=}CH_2$, $CH_2{-}C{\equiv}CH$,

$C(CH_3)_2{-}C{\equiv}CH$.

Organosilicon nitriles are obtained by condensing incompletely substituted silanes with alkenes[107,108]. Unsaturated nitriles react with silicochloroform and with alkylchlorosilanes:

$$CH_2{=}CH(CH_2)_n CN + CH_3SiCl_2H \xrightarrow[n\geqslant 1]{} (CH_3)Cl_2SiCH_2CH_2(CH_2)_n CN .$$

Petrov et al.[92] studied the addition of alkoxysilanes to but-3-enonitrile, β-allyloxypropionitrile, and acrylonitrile, and established that addition conforms to the equation

$$R'(RO)_2SiH + CH_2{=}CHCH_2X \rightarrow R'(RO)_2SiC_3H_4CH_2X$$

R′=CH_3, OC_2H_5, OCH_3; R=CH_3, C_2H_5; X=OCH_2CH_2CN, —CN.

Condensation of acrylonitrile, 2-vinylpyridine, and methacrylaldehyde with triethoxysilane and several other partly substituted silanes in the presence of activated AV-16 anion-exchange resin yields β-triethoxysilylpropionitrile and other silicon-containing nitriles[94-99].

Golubtsov et al.[93] investigated the reactions of methyldichlorosilane with acrylonitrile in the presence of various catalysts (pyridine, chloroplatinic acid), but did not achieve satisfactory results.

The action of a silicon–copper catalyst on β-chloropropionitriles forms β-trichlorosilylpropionitrile[101]:

$$ClCH_2CH_2CN \xrightarrow{Si/Cu} \begin{cases} \rightarrow HSiCl + SiCl_4 \\ \rightarrow CH_2{=}CH{-}CN \\ \rightarrow Cl_3SiCH_2CH_2CN \end{cases} .$$

Mono-, di-, and tri-nitriles containing chlorine attached to silicon have been obtained[102,103] directly from chloroacetonitrile, α-chloroacrylonitrile, and ω-chloromethacrylonitrile:

$$RCl \xrightarrow{Si/Cu} \begin{cases} \rightarrow HSiCl_3 + SiCl_4 \\ \rightarrow R_nSiCl_{4-n} \end{cases}$$

R=CH_2CN, $C(=CH_2){-}CN$, $CH_2{-}C(=CH_2){-}CN$; $n = 1$–3 .

These workers[103,104] examined the reactions of chlorosilylated nitriles, and have established[111] that silicon-containing nitriles can be obtained by condensation of a silanol with a chlorinated nitrile:

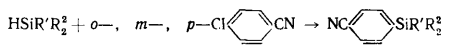
$$R_3SiOH + ClR'CN \rightarrow R_3SiOR'CN$$

R=CH_3; R′=$-CH_2-$, $-C(=CH_2)-$, $-CH_2-C(=CH_2)-CH_2-$, $-CH{=}CH-$, $-CH{=}C(CH_3)-$, $CH_3{-}CH{=}C<$.

The products can be converted by hydration into unsaturated organosilicon acids:

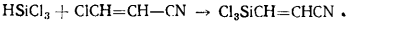
$$R_3SiOR'CN \xrightarrow[H_2SO_4]{HOH} R_3SiOR'COOH .$$

An original synthesis of organosilicon nitriles was suggested by Chernyshev and his coworkers[112,113]. *o*-, *m*-, and *p*-Trichlorosilylbenzonitriles and the corresponding methyldichlorosilyl compounds have been obtained[112] from a hydrolytic mixture of trichlorosilane or methyldichlorosilane with the appropriate chlorobenzonitrile in the gas phase at 500–650° C for a very short period of contact (10–90 s), after which the products were separated:

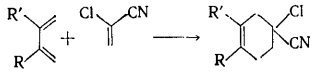


$R'=R^2=Cl$; $R'=CH_3$, $R^2=Cl$.

The same workers suggested[113] gas-phase pyrolysis of silicochloroform or methyldichlorosilane with β-chloroacrylonitrile or αβ-dichloroacrylonitrile at 500–650° C for 10–100 s to obtain the chlorosilylacrylonitriles:

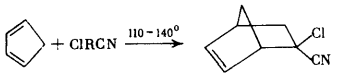


Like acrylonitrile chloro-derivatives of nitriles condense with dienes. The diene condensation of α-chloroacrylonitrile with butadiene, isoprene, etc. can be represented[87]



R=R'=H; R=H, R'=CH_3; R=H, R'=Cl; R=Cl, R'=CH_3; 'R=R'=Cl.

Bicyclic chloro-nitriles have been synthesised[106] by the diene condensation of α-chloroacrylonitrile and ω-chloromethacrylonitrile with cyclopentadiene:



R = $-C(=CH_2)$; $-CH_2-C(=CH_2)$.

The above survey shows that development of the preparation of chloro-derivatives of nitriles offers great promise, since the resulting monomers possess wide synthetic possibilities and have important applications.

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