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Development of the obtaining methods of substituted nitriles with useful properties

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Abstract
Nitrils and their derivatives always took detached place in the big family of organic compositions. The interest to these heteroatom containing organic compositions from one side is displaced with particular behavior in the reaction of organic synthesis due to C≡N grouping, from other side for the reason to display unique properties both the monomer itself and the products, and materials based on then.

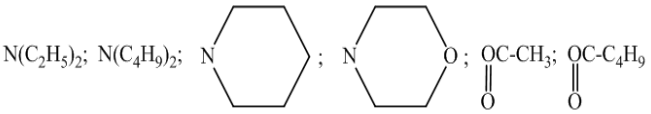
Keywords: nitrils, polymers, heteroatom, containing nitrils, monochlorine substituted nitrils, organo-nitrils complex

1. Introduction

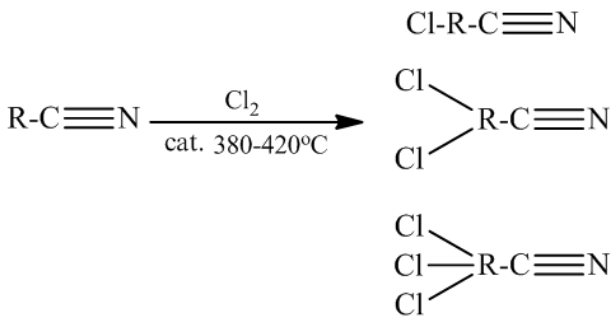
Substituted nitrils are flocculants of some metals, oxygene-clorine containing salts and decomposition inhibitors of non organic salts, particularly of mineral fertilizers [1]. Some hetero-atom containing nitrils have anti-corrosion properties, and also antimicrobe activity allowing to use substituted nitrils as biocorrosion inhibitors suppressing growth of fungi and bacteria. There is rather accessible synthesis method of derivative acrylonitrile- this is a reaction of addition of double hydrocarbon-hydrocarbon bond of alcohols, intial amines, fatty acids and etc. [2, 3].

$$CH_2=CH-C\equiv N + H - R' \xrightarrow{catalyst} R'CH_2-CH_2-C\equiv N$$

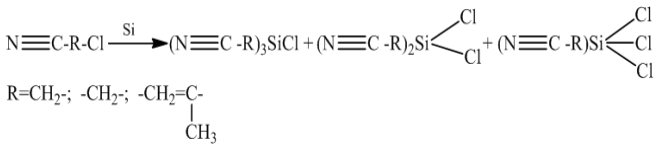
R'-OCH_3, OC_2H_5, OC_3H_7, OC_7H_9, OC_6H_5



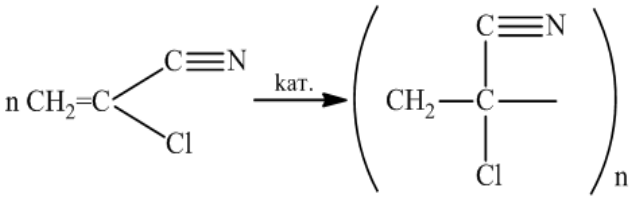
Here are only substituted maximum nitrils. Synthesis of monochlorine substituted nitrils is difficult. That's why we have used high-temperature synthesis of halogen substituted nitrils. Choice of chlorine halogen is explained by its industrial accessibility and cheapness. This methodics made it possible to obtain series of chlorine-substituted nitrils.



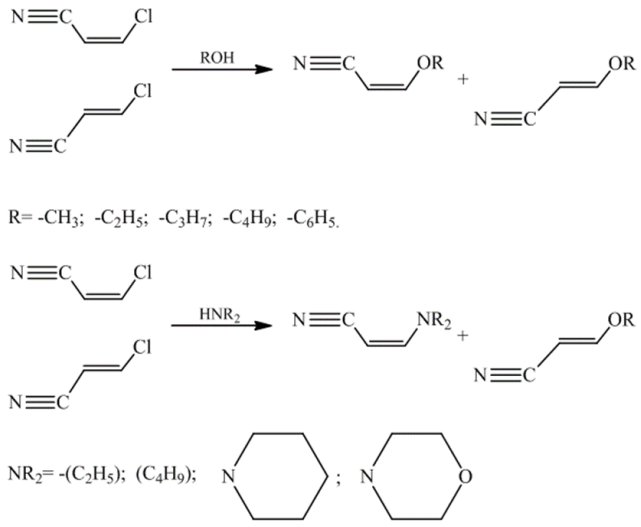
Structure and composition of chlorine substituted nitrils were proved by analysis and calculation using IR, PMR, NMR.
Monochlorine substituted nitrils presented great interest, not only from the point of view of solving a number of theoretical problems of organic synthesis, but also from obtaining of products with the given properties on their basis. According to analogues we have also used chlorine substituted nitrils in the reactions of nitro chlorine silanes synthesis.



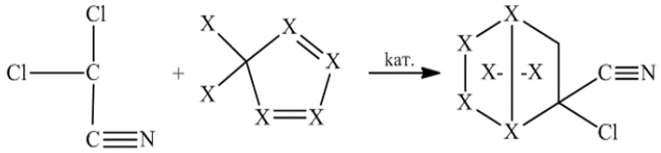
Obtaining of polymer with the content of atoms of silicon and cyanic group in its structure presented interest. With this purpose modification of octamethyltetracy closilox sane by acrylonitrile has been carried out by obtaining corresponding polymer. Analogously polymerization of a- chloroacry lonitrile in the presence of sour catalysts resulted to polymer formation with the content of chlorine atom and cyanic group and it formed fire-resistant, self-extinguishing polymer



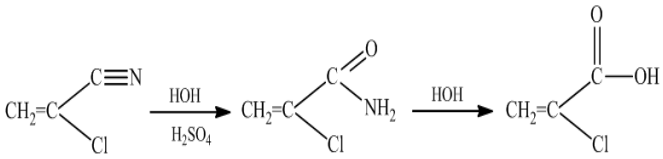
Obtaining of substituted nitrils based on their chlorine substituted analogues by nuclear Phil is of great interest, and it is mainly carried out in the mixture of trans-and sis-β-chlorine-acrylonitrile, and also by formation of isomer products mixture.



Chlorine substitution was also carried out in various nitrils inorganic salts. Cyclic and bicyclic nitrils substitution has been shown on the basis of Dils-Alder reaction.



The fact that drawing chlorine derivative nitrils into the hydrolysis reaction allowed to obtain corresponding amides and acids preserving chlorine atom.



Composition and structure of all obtained halogen substituted nitrils and their derivatives have been studied by physico-chemical methods of analysis.

Synthesis of new type amides and acids opens wide perspectiveness for obtaining of new type materials combining both frost-resistance and thermo-resistance, the main thing is that they reveal the obtaining ways of soluble polymers.

Formation of soluble complexes based on nitrils has been attracted the attention for recent 10-15 years, the result of which is wide investigation of nitrils.

Carrying out a number of reactions with involving nitrils, we especially used chlorines of the metals as the catalysts of reactions combining polymerization, day light and others. At the initial moment soluble complexes are formed, various colours depend on the nature of the salts of transition metals valency. In connection with it we studied the structure, physicochemical and applied properties of organonitril complexes of transition metals perspective as effective catalysts and additives to lubrication oils.

Coordination of the acrylonitrile chemistry is of special interest. This compound has important industrial significance and majority of its reactions at the initial stages are characterized by coordination interactions with Luis acids. Availability in the structure of acrylonitrile of double bond nitril group display properties of hard and soft Luis base conditions correspondingly possibility of its effective coordination with wide range of Luis acids. That's why our interest to acrylonitrile with the salts of transition metals is understandable. In this case we confined ourselves only with structure considering, but not chemical properties of the complexes. Organonitril complexes mainly form compounds with coordination bond through nitril group ("final" coordination).

That's why it is not suprising that compounds of this type very often were the object of the investigation. Organonitril complexes of transition metal with "final" coordination, structure of which determine of by X-ray structural diffraction method have been shown in table1.

According to the data of spectroscopic researches of complexes C≡H bond durability increases in the formation of coordination bond. It should be followed by some decrease of C≡H bond length in comparison with acetonenitril in coordination. The results of X-ray structural analysis are coordinated with these presentations.

Table 1: Structural parameters of nitrils complexes of transition metals with "final" coordination

Compound	Coal M-N-C (degree)	M-N (A)	N-C (A)
$Ticl_4$ (nccooet)$_2$	178.1	2.240	1.110
Vo (no_3)$_3$ (ncme)	180.0	2.240	1.170
$Vocl_3$ (ncme)	175.4	2.098	1.137
$Nbocl_3$ (ncme)$_2$	178.2	2.245	1.159
$Nbbr_4$ (ncme)$_2$	174.0	2.030	1.090
Wcl_4 (c_2cl_5n) ($ncccl_3$)	180.4	2.370	1.070
$Recl_3$ (pph_3)$_2$ (ncme)	175.4	2.050	1.170
$Recl_3$ (no) (ncme)	172.0	2.070	1.200
[$Asph_4$] [re(o) br_4 (ncme)]	170.0	2.310	1.220
[Net_4] [$rebr_4$ (no) (ncme)]	177.0	2.153	1.120
[Fe(ncme)] [$fecl_4$]	175.7	2.190	1.090
[Fe(ncet)$_5$cl] [$fecl_4$]$_2$	180.0	2.080	1.150
[Rh(c_2h_4)$_3$(ncme)$_2$] [bf_4]	180.0	1.980	1.210
Cu(no_3)$_2$ (ncme)$_2$	175.0	1.920	1.030
Cucl (ncme)	172.8	2.000	1.140
Cubr (ncme)	173.4	2.000	1.158
[Cu(ncch$_2$ch$_2$cn)$_2$]clo_4	169.7	2.987	1.180
[Cu(ncme)$_4$]clo_4	174.0	1.980	1.130

Spectroscopy plays significant role in determination of nitril-metal interaction type. Coordination effect in γ(CN) IR-spectres stripes of nitril complexes is traditionally used for determining their structure. It is considered that displacements to high frequencies determine "final" coordination of nitrils, but displacements to low frequencies characterize side coordination of nitrils. However, it became evident that "final" coordination can be caused by displacement γ(CN) both to high and low frequencies [4].

Coordination chemistry of nitrils, constituent part of substituted nitrils has also useful properties from the practical point of view. It should be noted that organonitril complexes

are the multifunctional additives to them giving to oils simultaneously anti-corrosion, anti-friction and microbe properties.

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