NITRILES

1. Introduction

Nitriles, or organic cyanides, are organic compounds that contain the cyano (ie, −CN) group. Nitriles are often considered derivatives of carboxylic acids and are named according to the carboxylic acid which is produced upon hydrolysis of the nitrile. For example, cyanomethane (methyl cyanide) is named acetonitrile [75-05-8] because hydrolysis of its cyano group yields acetic acid. Nitriles which contain additional functional groups are typically named as cyano-substituted compounds (eg, cyanoacetic acid). Nitriles which contain a hydroxy (−OH) group on the carbon atom that is bonded to the cyano moiety are known as cyanohydrins. According to *Chemical Abstracts*, aliphatic nitriles are named as derivatives of the longest carbon chain and the carbon of the nitrile is included.

2. General Preparations and Chemical Properties

Nitriles may be prepared by several methods (1). The first nitrile to be prepared was propionitrile, which was obtained in 1834 by distilling barium ethyl sulfate with potassium cyanide. This is a general preparation of nitriles from sulfonate salts and is referred to as the Pelouze reaction (2). Although not commonly practiced today, dehydration of amides has been widely used to produce nitriles and was the first commercial synthesis of a nitrile. The reaction of alkyl halides with sodium cyanide to produce nitriles (eq. 1) also is a general reaction with wide applicability:

$$RX + NaCN \rightarrow RCN + NaX \qquad (1)$$

where X = Cl, Br, or I. If dimethyl sulfoxide is used as solvent, high yields of nitriles can be obtained with both primary and secondary alkyl chlorides. This method also may be used for preparing dinitriles. Reaction times usually are less than one hour (3).

Ammoxidation, a vapor-phase reaction of hydrocarbon with ammonia and oxygen (air) (eq. 2), can be used to produce hydrogen cyanide (HCN), acrylonitrile, acetonitrile (as a by-product of acrylonitrile manufacture), methacrylonitrile, benzonitrile, and toluinitriles from methane, propylene, butylene, toluene, and xylenes, respectively (4).

$$RCH_3 + NH_3 + O_2 \xrightarrow{\text{catalyst}} RCN + H_2O \qquad (2)$$

Processes have been developed whereby the oxygen is supplied from the crystal lattice of a metal-oxide catalyst (5).

Addition of HCN to unsaturated compounds is often the easiest and most economical method of making organonitriles. An early synthesis of acrylonitrile involved the addition of HCN to acetylene. The addition of HCN to aldehydes and ketones is readily accomplished with simple base catalysis, as is the addition of HCN to activated olefins (Michael addition). However, the addition of HCN to

unactivated olefins and the regioselective addition to dienes is best accomplished with a transition-metal catalyst, as illustrated by DuPont's adiponitrile process (6–9).

3. Chemistry and Uses of Nitriles

As a class of compounds, nitriles have broad commercial utility that includes their use solvents, feedstocks, pharmaceuticals, and pesticides. The versatile reactivity of organonitriles arises both from the reactivity of the C≡N bond, and from the ability of the cyano substituent to activate adjacent bonds, especially C−H bonds. Nitriles can be used to prepare amines, amides, amidines, carboxylic acids and esters, aldehydes, ketones, large-ring cyclic ketones, imines, heterocycles, orthoesters, and other compounds. Some of the more common transformations involve hydrolysis or alcoholysis to produce amides, acids and esters, and hydrogenation to produce amines, which are intermediates for the production of polyurethanes and polyamides. An extensive review on hydrogenation of nitriles is available (10).

Acrylonitrile [107-13-1], the largest volume organonitrile, is an important monomer both for plastics and synthetic fibers. Acetonitrile, a by-product of acrylonitrile manufacture, is commercially important for solvent extraction, reaction media, and as an intermediate in the preparation of pharmaceuticals and other organic chemicals. Propionitrile [107-12-0], a by-product of the electrodimerization of acrylonitrile to adiponitrile, is used as a chemical intermediate. Hydrogenation of organonitriles to amines provides important intermediates both for polyurethanes (by way of isocyanates) and polyamides (nylons); adiponitrile is used almost exclusively by the manufacturers in the production of 1,6-diaminohexane (hexamethylenediamine), an intermediate for nylon-6,6. Other nitriles that are produced in thousands of metric tons per year include acetone cyanohydrin, 2-amino-2-methylpropionitrile, and fatty acid nitriles. Acetone cyanohydrin is an intermediate for the preparation of methyl methacrylate and arcylic resins, (eg, lucite and plexiglas) and for 5,5-dimethylhydantoin, which is used to make commercial water treatment chemicals. 2-Amino-2-methylpropionitrile is an intermediate for the preparation of azobis(isobutyronitrile), which is a widely used polymerization initiator (eg, Vazo 64) and in the production of some agrichemicals. Other aminonitriles are unisolated intermediates in the production of chelants such as ethylenediaminetetraacetate (EDTA) and nitrilotriacetate (NTA). The fatty acid nitriles are intermediates in the production of a large variety of commercial amines and amides. The nitriles that are commercially available in the United States and their manufacturers are listed in Table 1 (11). Global production of nitriles has increased significantly in the last twenty years. Excellent resources for identifying producers of organonitriles worldwide include Chem Sources International and SRI International's *Directory of Chemical Producers*.

4. General Health and Safety Factors

As a class of compounds, the two main toxicity concerns for nitriles are acute lethality and osteolathyrsm. A comprehensive review of the toxicity of nitriles, including detailed discussion of biochemical mechanisms of toxicity and structure–activity relationships, is available (12). Nitriles vary broadly in their ability to cause acute lethality and subtle differences in structure can greatly affect toxic potency. The biochemical basis of their acute toxicity is related to their metabolism in the body. Following exposure and absorption, nitriles are metabolized by cytochrome p450 enzymes in the liver. The metabolism involves initial hydrogen abstraction resulting in the formation of a carbon radical, followed by hydroxylation of the carbon radical. Metabolism at the carbon atom adjacent (alpha) to the cyano group would yield a cyanohydrin metabolite, which decomposes readily in the body to produce cyanide. Hydroxylation at other carbon positions in the nitrile does not result in cyanide release.

The propensity of nitriles to release cyanide subsequent to metabolism is the basis of their acute toxicity. Nitriles that form tertiary radicals at their alpha carbon atoms (eg, isobutyronitrile, 2-methylbutyronitrile) are substantially more acutely lethal than nitriles that form secondary radicals at their alpha carbons (eg, butyronitrile, propionitrile). Cyanohydrins are acutely toxic because they are unstable and release cyanide quickly. Alpha-aminonitriles are also acutely toxic, presumably by analogy with cyanohydrins.

Osteolathyrism is a disease characterized by lameness, skeletal deformities, aortic aneurysms, and slowing or cessation of body growth. Certain aminonitriles are known to cause osteolathyrism in several animal species; aminoacetonitrile, 3-aminopropionitrile, and 3-amino-2-methylpropionitrile are potent inducers of this disease. It is believed that the basis of their ability to cause osteolathyrism is due to their ability to inhibit lysine oxidase, an enzyme important in cross-linking of collagen and formation of connective tissue. While no reports of these substances causing osteolathyrism in humans have appeared, it seems plausible that these substances could cause this disease in humans because they are known to cause it in a variety of experimental animals.

Persons handling nitriles should take precautions to prevent inhalation of fumes or skin contact. Butyl rubber gloves are frequently used because they resist permeation by many nitriles more efficiently than most gloves. Inhalation may cause headache, nausea, vomiting, irritation of mucosal membranes, and dizziness. Skin contact may result in similar symptoms, but may develop more slowly. Other symptoms of cyanide poisoning include rapid pulse, flushing of the skin, and initial rapid respiration followed by labored breathing. A person who has inhaled the vapors should be moved to an uncontaminated environment, and cardiopulmonary resuscitation should be administered if necessary. If the victim breathes with difficulty, oxygen should be given. In case of eye contact flush with copious water for at least 20 min and call a physician. In case of ingestion, induce vomiting and call a physician. For skin contact, wash with plenty of soap and water. In each case, observe victim for several hours for delayed reaction due to metabolism or decomposition in the body.

5. Acetonitrile

Acetonitrile (ethanenitrile), CH_3CN, is a colorless liquid with a sweet, ethereal odor. Its physical properties are listed in Table 2. It is completely miscible with water and its high dielectric strength and dipole moment make it an excellent solvent for both inorganic and organic compounds including polymers. Some representative inorganic compounds that are soluble in acetonitrile are $CaCl_2$, CuCl, $FeCl_2$, $FeCl_3$, KSCN, $KMnO_4$, $AgNO_3$, and $ZnCl_2$. Many gases also are highly soluble in acetonitrile, eg, olefinic hydrocarbons, halides, HCl, SO_2, and H_2S. It forms low boiling azeotropes with many organics and high boiling azeotropes with BF_3, $SiCl_4$, and $(CH_3)_4Pb$ (13). Some of its azeotropes are listed in Table 3 (14).

Although acetonitrile is one of the more stable nitriles, it undergoes typical nitrile reactions and is used to produce many types of nitrogen-containing compounds, eg, amides (15), amines (16,17); higher molecular weight mono- and dinitriles (18,19); halogenated nitriles (20); ketones (21); isocyanates (22); heterocycles, eg, pyridines (23), and imidazolines (24). It can be trimerized to *s*-trimethyltriazine (25) and has been telomerized with ethylene (26) and copolymerized with α-epoxides (27).

Most, if not all, of the acetonitrile that was produced commercially in the United States in 1995 was isolated as a by-product from the manufacture of acrylonitrile by propylene ammoxidation. The amount of acetonitrile produced in an acrylonitrile plant depends on the ammoxidation catalyst that is used, but the ratio of acetonitrile:acrylonitrile usually is ca 2–3:100. A process increasing the yield of acetonitrile during the manufacture of acrylonitrile using a moisture of ketones has been reported (28). The acetonitrile is recovered as the water azeotrope, dried, and purified by distillation (29,30).

Specifications for commercial acetonitrile are given in Table 4. The principal organic impurity in commercial acetonitrile is propionitrile; although small amounts of allyl alcohol also may be present.

5.1. Shipping and Storage. The DOT/IMO classification for acetonitrile is class 3 hazard, UN No. 1648. It requires a FLAMMABLE LIQUID label on all containers and is in packing group II. For storage and piping at normal temperatures and pressures, aluminum or carbon steel may be used. Centrifugal pumps are preferred because the solvency of acetonitrile may affect the lubricant in positive-displacement pumps. All tanks, piping valves, and pumps should be electrically grounded. Fire protection equipment call be water spray, alcohol foam, CO_2, or dry chemical.

5.2. Health and Safety Factors. The following toxicities for acetonitrile have been reported: oral LD_{50} (rats), 3030–6500 mg/kg; skin LD_{50} (rabbits), 3884–7850 mg/kg; and inhalation LC_{50} (rats), 7500–17,000 ppm (31). Humans can detect the odor of acetonitrile at 40 ppm. Exposure for 4 h at up to 80 ppm has not produced adverse effects. However, exposure for 4 h at 160 ppm results in reddening of the face and some temporary bronchial tightness.

Although acetonitrile has a low order of acute toxicity by ingestion, inhalation, and skin absorption, it can cause severe eye burns. In case of eye contact, eyes should be immediately flushed with water for at least 15 min and a

physician should be consulted. In the event of a spill or leak, the spill should be contained, flooded with water, and disposed of according to local regulations. Acetonitrile is flammable (see Table 2) and must be kept away from excessive heat, sparks, and open flame. Associated fires can be extinguished using water spray, alcohol foam, CO_2, or dry chemical extinguishers. OSHA requires that an employee's exposure to acetonitrile in any 8-h shift does not exceed a time-weighted average of 40 ppm (70 mg/m^3) in air (32). NIOSH (TWA) is 34 mg/m^3 (33).

5.3. Uses. Because of its good solvency and relatively low boiling point, acetonitrile is used widely as a recoverable reaction medium, particularly for the preparation of pharmaceuticals. Its largest use is for the separation of butadiene from C_4 hydrocarbons by extractive distillation (34). It also has been proposed for the separation of other olefins, eg, propylene, isoprene, allene, and methylacetylene from hydrocarbon streams (35–37). It is a superior solvent for polymers and can be used as a solvent for spinning fibers and for casting and molding plastics. It is used widely in spectrophotometry and electrochemistry. Since pure acetonitrile does not absorb uv light, it is commonly used as a solvent in high pressure liquid chromatography (hplc) for the detection of materials, eg, residual pesticides, in the ppb range; highly purified hplc grade acetonitrile is routinely available from suppliers.

Acetonitrile also is used as a catalyst and as an ingredient in transition-metal complex catalysts (38,39). There are many uses for it in the photographic industry and for the extraction and refining of copper and by-product ammonium sulfate (40–42). It also is used for dyeing textiles and in coating compositions (43,44). It is an effective stabilizer for chlorinated solvents, particularly in the presence of aluminum, and it has some application in the manufacture of perfumes (45,46). It also is used as a reagent for the preparation of a wide variety of compounds.

6. Adiponitrile

Adiponitrile (hexanedinitrile, dicyanobutane, ADN), $NC(CH_2)_4CN$, is manufactured principally for use as an intermediate for hexamethylenediamine (1,6-diaminohexane), which is a principal ingredient for nylon-6,6. However, in 1996, BASF announced the development of a process to make caprolactam from adiponitrile (47,48). Caprolactam is used to produce nylon-6.

Pure adiponitrile is a colorless liquid and has no distinctive odor; some properties are shown in Table 5. It is soluble in methanol, ethanol, chloroalkanes, and aromatics but has low solubility in carbon disulfide, ethyl ether, and aliphatic hydrocarbons. At 20°C, the solubility of adiponitrile in water is ca 8 wt%; the solubility increases to 35 wt% at 100°C. At 20°C, adiponitrile dissolves ca 5 wt% water.

Adiponitrile undergoes the typical nitrile reactions, eg, hydrolysis to adipamide and adipic acid and alcoholysis to substituted amides and esters. The most important industrial reaction is the catalytic hydrogenation to hexamethylenediamine. A variety of catalysts are used for this reduction including cobalt–nickel (49), cobalt manganese (50), cobalt boride (51), copper cobalt (52), and

iron oxide (53), and Raney nickel (54). An extensive review on the hydrogenation of nitriles has been published (10).

Adiponitrile is made commercially by several different processes utilizing different feedstocks. The original process, utilizing adipic acid as a feedstock, was first commercialized by DuPont in the late 1930s and was the basis for a number of adiponitrile plants. However, the adipic acid process was abandoned by DuPont in favor of two processes based on butadiene. During the 1960s, Monsanto and Asahi developed routes to adiponitrile by the electrodimerization of acrylonitrile.

The reaction of adipic acid with ammonia in either liquid or vapor phase produces adipamide as an intermediate which is subsequently dehydrated to adiponitrile. The most widely used catalysts are based on phosphorus-containing compounds, but boron compounds and silica gel also have been patented for this use (55–59). Vapor-phase processes involve the use of fixed catalyst beds; whereas, in liquid–gas processes, the catalyst is added to the feed. The reaction temperature of the liquid-phase processes is ca 300°C and most vapor-phase processes run at 350–400°C. Both operate at atmospheric pressure. Yields of adipic acid to adiponitrile are as high as 95% (60).

In the now-obsolete furfural process, furfural was decarboxylated to furan which was then hydrogenated to tetrahydrofuran (THF). Reaction of THF with hydrogen chloride produced dichlorobutene. Adiponitrile was produced by the reaction of sodium cyanide with the dichlorobutene. The overall yield from furfural to adiponitrile was around 75%.

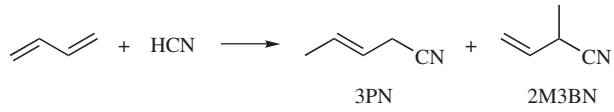
In a related process, 1,4-dichlorobutene was produced by direct vapor-phase chlorination of butadiene at 160–250°C. The 1,4-dichlorobutenes reacted with aqueous sodium cyanide in the presence of copper catalysts to produce the isomeric 1,4-dicyanobutenes; yields were as high as 95% (61). The by-product NaCl could be recovered for reconversion to Na and Cl_2 via electrolysis. Adiponitrile was produced by the hydrogenation of the dicyanobutenes over a palladium catalyst in either the vapor phase or the liquid phase (62,63). The yield in either case was 95% or better. This process is no longer practiced by DuPont in favor of the more economically attractive process described below.

DuPont currently practices a butadiene-to-adiponitrile route based on direct addition of HCN to butadiene (6–9). It was first commercialized in 1971. All reactions are catalyzed by soluble, air and moisture sensitive, triarylphosphite-nickel(0) complexes.

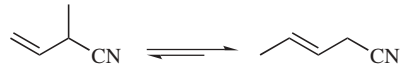
The first HCN addition (eq. 3) occurs at practical rates above 70°C under sufficient pressure to keep butadiene condensed in solution and produces the 1,4- and 1,2-addition products (3-pentenenitrile [4635-87-4], 3PN, and 2-methyl-3-butenenitrile [16529-56-9], 2M3BN) in a 2 to 1 ratio. Fortunately, thermodynamics favors 3PN (about 20:1) and 2M3BN may be isomerized to 3PN (eq. 4) in the presence of a nickel catalyst.

The selective addition of the second HCN to provide ADN requires the concurrent isomerization of 3PN to 4-pentenenitrile [592-51-8], 4PN (eq. 5), and HCN addition to 4PN (eq. 6). A Lewis acid promoter is added to control selectivity and increase rate in these latter steps. Temperatures in the second addition are significantly lower and practical rates may be achieved above 20°C at atmospheric pressure. A key to the success of this homogeneous catalytic

process is the ability to recover the nickel catalyst from product mixture by extraction with a hydrocarbon solvent. 2-Methylglutaronitrile [4553-62-2], MGN, ethylsuccinonitrile [17611-82-4], ESN, and 2-pentenenitrile [25899-50-7], 2PN, are by-products of this process and are separated from adiponitrile by distillation. DuPont has developed chelating diphosphite–nickel catalysts for this technology which are significantly more active than the older monodentate phosphite based catalyst system used for this process (64–67).

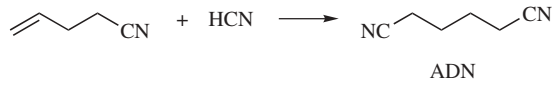


3PN 2M3BN (3)

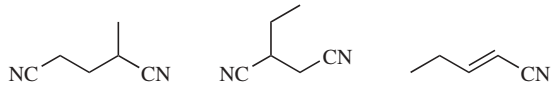


(4)

4PN (5)



ADN



MGN ESN 2PN (6)

The Monsanto adiponitrile process, first commercialized in 1965 (68–70), involves the dimerization of acrylonitrile at the cathode in an electrolytic cell (eq. 7):

$$2\,CH_2{=}CHCN + 2\,H^+ + 2\,e \rightarrow NC(CH_2)_4CN \qquad (7)$$

Small amounts of propionitrile and bis(cyanoethyl) ether are formed as by-products. The hydrogen ions are formed from water at the anode and pass to the cathode through a membrane. The catholyte that is continuously recirculated in the cell consists of a mixture of acrylonitrile, water, and a tetraalkylammonium salt; the anolyte is recirculated aqueous sulfuric acid. A quantity of catholyte is continuously removed for recovery of adiponitrile and unreacted acrylonitrile; the latter is fed back to the catholyte with fresh acrylonitrile. Oxygen that is produced at the anodes is vented and water is added to the circulating anolyte to replace the water that is lost through electrolysis. The operating temperature of the cell is ca 50–60°C. Current densities are 0.25–1.5 A/cm^2.

A typical composition of the catholyte is adiponitrile, 15 wt%; acrylonitrile, 15 wt%; quaternary ammonium salt, 39 wt%; water, 29 wt%; and by-products, 2 wt%. Such a solution is extracted with acrylonitrile and water, which separates

the organics from the salt that can be returned to the cell. The acrylonitrile is distilled from the extract and the resultant residue consists of ca 91 wt% adiponitrile, which is purified further by distillation. The overall yield of acrylonitrile to adiponitrile is 92–95%.

6.1. Shipment. The DOT/IMO classification for adiponitrile is class 6.1 hazard, UN No. 2205. It requires a POISON label on all containers and is in packing group III. Approved materials of construction for shipping, storage, and associated transportation equipment are carbon steel and type 316 stainless steel. Either centrifugal or positive displacement pumps may be used. Carbon dioxide or chemical-foam fire extinguishers should be used. There are no specifications for commercial adiponitrile. The typical composition is 99.5 wt% adiponitrile. Impurities that may be present depend on the method of manufacture, and thus, vary depending on the source.

6.2. Health and Safety Factors. See "General Health and Safety Factors." The following toxicities for adiponitrile have been reported: oral LD_{50} (rats), 300 mg/kg; dermal LD_{50} (rabbits), 2,134 mg/kg; and inhalation 4-h LC_{50} (rats), 1.7 mg (71). NIOSH TWA is 18 mg/m^3 ACGIN TLV is 2 ppm (sken) (33).

6.3. Uses. The principal use of adiponitrile is for hydrogenation to hexamethylene diamine leading to nylon-6,6. However, as a result of BASF's adiponitrile-to-caprolactam process, a significant fraction of ADN produced has found its way into nylon-6 production. A process to produce hexamethylene from adiponitrile where the hexamethylene contains less than 100 ppm of the by-product tetrahydroazepine has been reported (72). Adipoquanamine, which is prepared by the reaction of adiponitrile with dicyandiamide [461-58-5] (cyanoguanidine), may have uses in melamine–urea amino resins. Its typical liquid nitrile properties suggest its use as an extractant for aromatic hydrocarbons.

7. α-Aminonitriles

α-Aminonitriles are compounds containing both cyano and amine substituents attached to the same carbon atom. They are versatile synthetic intermediates that are used to make aminoacids, agrichemicals, chelants, radical initiators, and water-treatment chemicals. In some cases, aminonitriles produced as intermediates are not isolated, but immediately further reacted, for example by hydrolysis, as is the case in producing ethylenediaminetetraacetate (EDTA) or nitrilotriacetate (NTA). Isolated and commercially available aminonitriles include 2-amino-2-methylpropanenitrile (aminoisobutyronitrile, AN-64) [19355-69-2], 2-amino-2-methylbutanenitrile (AN-67) [4475-95-0], 2-amino-2,4-dimethylpentanenitrile (AN-52) [26842-43-3], and 1-aminocyclohexane carbonitrile(AN-88) [5496-10-6]. The designation in parentheses arise from their identity as intermediates in the production of azo radical initiators (see below).

Historically these compounds have been made in two-step processes. For smaller volumes, reaction of an appropriate ketone or aldehyde with a cyanide salt followed by treatment with an ammonium salt proves satisfactory (Strecker synthesis). For larger volumes, treatment of the ketone or aldehyde with HCN to produce a cyanohydrin, followed by treatment with ammonia has been practiced.

However, in 1990, DuPont began practicing a one-step process (73) in which the a ketone is treated simultaneously with both HCN and ammonia at 40–60°C. The process, based on the understanding that a cyanohydrin is not on the reaction pathway (Fig. 1), is both faster and more selective. The uncatalyzed reactions are driven to completion by the presence of excess ammonia; water is a by-product. If excess ammonia is removed without separating the by-product water, the reaction may be reversed to produce the reagents. Therefore, these products are often stored and shipped in the presence of excess ammonia.

7.1. Physical Properties. α-Aminonitriles are stable at modest temperatures (<70°C) in the absence of water; in the presence of water, they can degrade to their original constituents, ie, ketone (aldehyde), ammonia and hydrogen cyanide if insufficient ammonia is present. For this reason they are frequently stored in the presence of excess ammonia. Even in the presence of ammonia, aminonitriles begin to degrade at temperatures above 70°C, depending on the pressure of ammonia. The aminonitriles based on ketones described here are clear colorless liquids, but sometimes appear yellow to brown depending on the synthetic procedure and the amount of decomposition. They are soluble in polar organic solvents and in aromatic solvents. AN-64, AN-67, and AN-88 are soluble in water; AN-52 is insoluble in water. They have an ammonia-like odor. Vapor pressure of pure aminonitriles are AN-64, 4 kPa (30 torr) at 66°C; AN-67, 1.9 kPa (14 torr) at 68°C; AN-52, 66 Pa (0.5 torr) at 70°C and 267 Pa (2 torr) at 84°C; AN-88, 200–400 Pa (1.5–3 torr) at 82°C. Specific gravity is about 0.9 for AN-64, -67, and -52, and 1.03 for AN-88.

7.2. Shipment. The DOT/IMO shipping information is shown in Table 6. Approved materials of construction for shipping, storage, and associated transportation equipment are lined carbon steel (DOT spec. 105 S 500W) and type 316 stainless steel. Water spray, carbon dioxide, chemical-foam, or dry-chemical fire extinguishers may be used.

7.3. Health and Safety Factors. See "General Health and Safety Factors." As a class, alpha-aminonitriles are exceedingly acutely lethal from oral, inhalation, dermal, and occular exposure. Some are known to cause osteolathyritic effects in experimental animals. The following toxicology data have been reported for the aminonitriles reported here. AN-64: oral LD_{50} (rats) 45 mg/kg, inhalation LC_{50} (rats) 112 ppm; AN-67: inhalation LC_{50} (rats) 111 ppm; AN-52: inhalation LC_{50} (rats) 100 ppm, dermal LD_{50} (rabbits) 90 mg/kg; AN-88: oral LD_{50} (rats) 200 mg/kg, inhalation LC_{50} (rats) 161 ppm, dermal LD_{50} (rabbits) <200 mg/kg. Additional data for these and other aminonitriles are available (12). These compounds are frequently stabilized with excess ammonia and thermal decomposition leads to the evolution of both ammonia and hydrogen cyanide. Accordingly, first-aid treatment should be consistent with both ammonia and cyanide exposure. In case of ingestion, drink two glasses of water and induce vomiting and call a physician (DO NOT give Syrup of Ipecac). Spills should be contained and treated with dry sodium bicarbonate ($NaHCO_3$) to absorb the spilled aminonitrile and make a dry solid at a ratio of three (3) pounds of $NaHCO_3$ per pound of aminonitrile. Transfer aminonitrile/$NaHCO_3$ solids to plastic or metal drums for disposal. Firefighters may use water, carbon dioxide, dry-chemical or chemical foam extinguishers and should wear self-contained breathing apparatus.

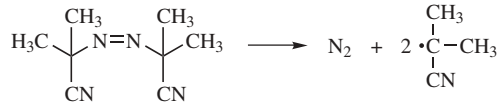
7.4. Uses. α-Aminonitriles may be hydrolyzed to aminoacids, such as is done in producing ethylenediaminetetracetate (EDTA) or nitrilotriacetate (NTA). In these cases, formaldehyde is utilized in place of a ketone in the synthesis. The principal use of the ketone-based aminonitriles described above is in the production of azobisnitrile radical initiators (see below). AN-64 is also used as an intermediate in the synthesis of the herbicide Bladex. Aminonitriles are also excellent intermediates for the synthesis of substituted hydantoins by reaction with carbon dioxide; however, this is not currently commercially practiced.

8. Azobisnitriles

Azobisnitriles are efficient sources of free radicals for vinyl polymerizations and chain reactions, eg, chlorinations. These compounds decompose in a variety of solvents at nearly first-order rates to give free radicals with no evidence of induced chain decomposition. They can be used in bulk, solution, and suspension polymerizations, and because no oxygenated residues are produced, they are suitable for use in pigmented or dyed systems that may be susceptible to oxidative degradation.

DuPont (D) and/or Wako (W) produce several members of this class of compounds: 2,2′-azobis(isobutyronitrile) [78-67-1] (Vazo 64 (D); V-60 (W)); 2,2′-azobis(2-methylbutanenitrile) [13472-08-7] (Vazo 67 (D); V-59 (W)); 2,2′-azobis(2,4-dimethylpentanenitrile) [4419-11-8] [Vazo 52 (D); V-65 (W)]; 1,1′-azobis (cyanocyclohexane) [2094-98-6] [Vazo 88 (D)]; and 2,2′-azobis(4-methoxy-2,4-dimethylpentanenitrile [15545-97-8] (V-70 (W)). They are crystalline solids that are produced by hypochlorite oxidation of α-aminonitriles (74). Physical properties are listed in Table 7 (75,76). These compounds are essentially insoluble in water, sparingly soluble in aliphatic hydrocarbons, and soluble in functional compounds and aromatic hydrocarbons.

In solution, the azobisnitriles decompose on heating to form two free radicals with the liberation of nitrogen (eq. 8):



(8)

Because the decomposition is first order, the rate of free-radical formation can be controlled by regulating the temperature; equations relating half-life to temperature are provided in Table 7. These decomposition rates are essentially independent of the solvent (73).

8.1. Shipping and Storage. DOT/IMO shipping information for Vazo products are provided in Table 8. Vazo polymerization initiators must be stored out of the sun and away from heat in a cool, dry place. Since decomposition produces nitrogen and, consequentially, a pressure increase, these compounds should not be stored in glass or in any tightly closed containers other than the original shipping container. The maximum storage temperatures are provided in Table 7.

8.2. Health and Safety Factors. Some of the Vazo products are mild skin or eye irritants in laboratory animals (Table 9) but none are skin sensitizers. In the absence of a polymerizable vinyl polymer, tetramethylsuccinonitrile [3333-52-6] (TMSN) is the principal decomposition product of Vazo 64. TMSN is highly toxic orally (rat oral LD_{50} of 39 mg/kg) and by inhalation (29). OSHA regulations require that an employee's exposure to TMSN in any 8-h shift does not exceed an 8-h time-weighted average of 0.5 ppm in air ($= 3$ mg/m^3). Because both TMSN solid and vapor are capable of penetrating the skin and mucous membranes, control of vapor inhalation alone may not be sufficient to prevent absorption of an excessive dose.

All operations should be carried out with good ventilation and contact with eyes and skin should be avoided. In case of eye contact, the eyes should be flushed with water for 15 min and a physician should be consulted. Soap and water should be used to wash azobisnitriles from skin. If these compounds are inhaled, particularly the decomposition products of Vazo 64, the victim should be removed to fresh air and oxygen should be administered. If the victim is not breathing, cardiopulmonary resuscitation should be administered. A physician should be called in either case. Small quantities of waste Vazo should be disposed of by incineration, preferably by dissolving first in a waste liquid. Large quantities of waste Vazo should be returned to the manufacturer for disposal.

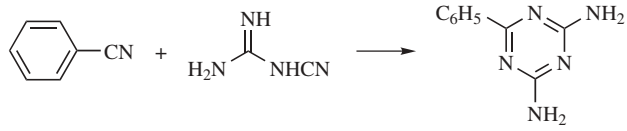
8.3. Uses. The azobisnitriles have been used for bulk, solution, emulsion, and suspension polymerization of all of the common vinyl monomers, including ethylene, styrene vinyl chloride, vinyl acetate, acrylonitrile, and methyl methacrylate. The polymerizations of unsaturated polyesters and copolymerizations of vinyl compounds also have been initiated by these compounds.

9. Benzonitrile

Benzonitrile [100-47-0], C_6H_5CN, is a colorless liquid with a characteristic almondlike odor. Its physical properties are listed in Table 10. It is miscible with acetone, benzene, chloroform, ethyl acetate, ethylene chloride, and other common organic solvents but is immiscible with water at ambient temperatures and soluble to ca 1 wt% at 100°C. It distills at atmospheric pressure without decomposition, but slowly discolors in the presence of light.

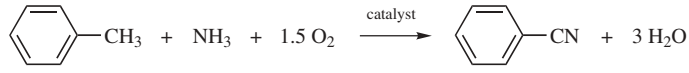
Like acetonitrile, benzonitrile is a powerful solvent for many inorganic and organic materials including some polymers. Inorganic salts that are soluble in benzonitrile at 25°C include aluminum chloride, ferric chloride, and silver nitrate. In chemical reactions, benzonitrile displays characteristics of both the nitrile group and the aromatic nucleus. It can be converted to a large number and variety of derivatives by simple syntheses; eg, by hydrolysis, it can be converted to either benzoic acid or benzamide. Hydrolysis in the presence of $ZnCl_2$ and HCl produces benzaldehyde, whereas alcoholysis leads to the formation of benzoic acid esters. Reduction produces benzyl- or dibenzylamine and reductive alkylation produces *N*-substituted benzamides. The aromatic ring can be halogenated or nitrated without the nitrile group being affected. Benzonitrile can be trimerized in the presence of a catalytic amount of base to 2,4,6-triphenyl-

1,3,5-triazine (78). The most important reaction is with dicyandiamide to produce 2,4-diamino-6-phenyl-1,3,5-triazine (benzoguanamine) (eq. 9) (79):



(9)

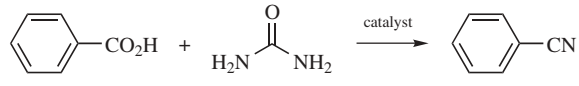
Benzonitrile can be produced in high yield by the vapor-phase catalytic ammoxidation of toluene (eq. 10) (80):



(10)

An older route is based on just toluene and ammonia in the absence of air with separate catalyst regeneration (81).

In 1987, Toray Industries, Inc., announced the development of a new process for making aromatic nitriles which reportedly halved the production cost, reduced waste treatment requirements, and reduced production time by more than two-thirds, compared with the vapor-phase process used by most producers. The process involves the reaction of benzoic acid (or substituted benzoic acid) with urea at 220–240°C in the presence of a metallic catalyst (eq. 11) (82).



(11)

A method for making benzonitrile by dehydrogenation of the Diels-Alder adduct of butadiene and acrylonitrile also has been described (83). Benzonitrile also can be made on a small scale by the dehydration of benzamide in an inert solvent with phosphorus oxychloride or benzenesulfonyl chloride and an organic amine (84,85).

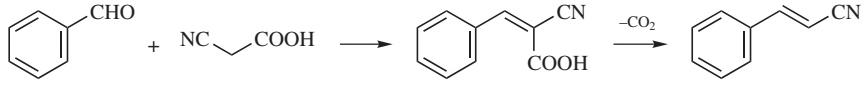
9.1. Shipping and Storage. The DOT hazard classification for BENZONITRILE is "Flammable", UN No. 2224. Carbon-steel drums and tanks may be used for storage.

9.2. Health and Safety Factors. See "General Health and Safety Factors." The following toxicities for benzonitrile have been reported: oral LD_{LO} (rats), 720 mg/kg; skin LD_{50} (rats), 1200 mg/kg; and inhalation LC_{50} (rats), 950 ppm/8 h.

9.3. Uses. The most important commercial use for benzonitrile is the synthesis of benzoguanamine, which is a derivative of melamine and is used in protective coatings and molding resins. Other uses for benzonitrile are as an additive in nickel-plating baths, for separating naphthalene and alkylnaphthalenes from nonaromatics by azeotropic distillation, as a jet-fuel additive, in cotton bleaching baths, as a drying additive for acrylic fibers, and in the removal of titanium tetrachloride and vanadium oxychloride from silicon tetrachloride.

10. Cyanoacetic Acid and Esters

The physical properties of cyanoacetic acid [372-09-8] and two of its ester derivatives are listed in Table 11 (86). The parent acid is a strong organic acid with a dissociation constant at 25°C of 3.36×10^3. It is prepared by the reaction of chloroacetic acid with sodium cyanide. It is hygroscopic and highly soluble in alcohols and diethyl ether but insoluble in both aromatic and aliphatic hydrocarbons. It undergoes typical nitrile and acid reactions but the presence of the nitrile and the carboxylic acid on the same carbon cause the hydrogens on C-2 to be readily replaced. The resulting malonic acid derivative decarboxylates to a substituted acrylonitrile (eq. 12):



(12)

cinnamonitrile
[*4360-47-8*]

The methyl and ethyl esters of cyanoacetic acid are slightly soluble in water but are completely miscible in most common organic solvents including aromatic hydrocarbons. The esters, like the parent acid, are highly reactive, particularly in reactions involving the central carbon atom; however, the esters tend not to decarboxylate. They are prepared by esterification of cyanoacetic acid and are used principally as chemical intermediates.

10.1. Health and Safety Factors. The following toxicities have been reported for cyanoacetic acid: oral LD_{50} (rat) 1500 mg/kg; subcutaneous LD_{LO} (rabbit), 1900 mg/kg; and subcutaneous LD_{LO} (frog); 1300 mg/kg (29). For ethyl cyanoacetate the following toxicities have been reported: interperitoneal LD_{50} (mice), 750 mg/kg; subcutaneous LD_{LO} (rabbits), 1500 mg/kg; and subcutaneous LD_{LO} (frogs), 4000 mg/kg.

10.2. Uses. Although cyanoacetic acid can be used in applications requiring strong organic acids, its principal use is in the preparation of malonic esters and other reagents used in the manufacture of pharmaceuticals, eg, barbital, caffeine, and B vitamins. Cyanoacetic acid can be used for the preparation of heterocyclic ketones.

11. Isophthalonitrile

Isophthalonitrile [626-17-5] (1,3-dicyanobenzene, IPN), is a white solid which melts at 161°C and sublimes at 265°C. It is slightly soluble in water but readily dissolves in dimethylformamide, *N*-methylpyrrolidinone and hot aromatic solvents. IPN undergoes the reactions expected of an aromatic nitrile, eg, hydrogenation of both nitrile groups and aromatic ring and chlorination to tetrachloroisophthalonitrile. IPN is prepared by vapor-phase ammoxidation of *meta*-xylene. The oral LD_{50} for rats is 860 mg/kg. Its principal use appears to

be as an intermediate to amines. As a reagent, IPN can be used to convert aromatic acids to nitriles in near quantitative yields (87).

12. 2-Methylglutaronitrile

Methylglutaronitrile (2,3-dicyanobutane) [4553-62-2], MGN, is a by-product of DuPont's adiponitrile process. The oral LD_{50} (rats) is 400 mg/kg (29). Some physical properties are listed in Table 12.

12.1. Shipping and Storage. The DOT shipping name for MGN is "Toxic liquid, Organic, N. O. S. (Methylglutaronitrile)" and is in the hazard class 6.1, packing group III, UN 2810. It requires a "POISON" label. Carbon-steel drums and tanks may be used for storage.

12.2. Uses. Methylglutaronitrile is readily hydrogenated to give 2-methyl-1,5-pentanediamine (DYTEK A, MPMD), used as a comonomer in polyamide fibers and resins, as a curing agent for epoxy coatings, and as its isocyanates in specialty urethanes. A co-product of the DYTEK A process is 3-methylpiperidine which can be used to produce vulcanization accelerators for rubber curing or can be converted to 3-picoline, an intermediate used to make niacin and niacinamide. 3-Picoline may also be made by direct conversion of MGN or alternatively from DYTEK A.

13. Pentenenitriles

Pentenenitriles are produced as intermediates and by-products in DuPont's adiponitrile process. 3-Pentenenitrile [4635-87-4], is the principal product isolated from the isomerization of 2-methyl-3-butenenitrile (see eq. 4). It is entirely used to make adiponitrile. *cis*-2-Pentenenitrile [25899-50-7], is a by-product isolated from the second hydrocyanation step. Some physical properties are listed in Table 13.

13.1. Shipping and Storage. The DOT shipping name for 2[3]-pentenenitrile is "Toxic liquid, Flammable, Organic, N. O. S. (2[3]-Pentenenitrile)" and is in the hazard class 6.1, packing group II, UN 2929. It requires a "POISON, FLAMMABLE" label. Carbon-steel drums and tanks may be used for storage.

13.2. Health and Safety Factors. See "General Health and Safety Factors." The following toxicities for 2-pentenenitrile have been reported: dermal, LD_{50} (rabbit) >200 mg/kg; oral LD_{LO} (rat) 450 mg/kg; 4-hr Inhalation LC_{50} (rats) 740 ppm (29).

13.3. Uses. 3-Pentenenitrile, 3PN, is used entirely by the manufacturers to make adiponitrile. *cis*-2-Pentenenitrile, 2PN, can be cyclized catalytically at high temperature to produce pyridine, a solvent and agricultural chemical intermediate. 2PN is also chlorinated to manufacture pentachloropyridine, an intermediate in the insecticide Dursban produced by Dow. Addition of ammonia to 2PN followed by reduction leads to 1,3-pentadiamine (Dytek ep), which is used as a curing agent for epoxy coatings and as a chain modifier in polyurethanes.

14. Fatty Acid Nitriles

Some of the physical properties of fatty acid nitriles are listed in Table 14. Fatty acid nitriles are produced as intermediates for a large variety of amines and amides. Fatty acid nitrile sare produced from the corresponding acids by a catalytic reaction with ammonia in the liquid phase. They have little use other than as intermediates but could have some utility as surfactants, rust inhibitors, and plasticizers.

15. Disclaimer

This article has been reviewed by the Office of Environmental Information, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of commercial products or synthesis constitute endorsement or recommendation for use.

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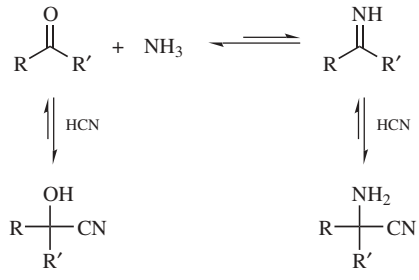

Fig. 1. Reactive pathway for α-aminonitriles synthesis.

Table 1. **Commercially Available Nitriles in the United States, 1994**[a]

Nitriles	CAS Registry Number	Manufacturers
acetone cyanohydrin	[75-86-5]	BP Chemicals, CYRO, ICI, Rohn & Hass
acetonitrile	[75-05-8]	BP Chemicals, Cytec, DuPont, JT Baker, Sterling
acrylonitrile	[107-13-1]	BP Chemicals, Cytec, DuPont, Monsanto, Sterling, Witco
adiponitrile	[111-69-3]	DuPont, Monsanto
2-amino-2-methylpropanenitrile	[19355-69-2]	Degussa, DuPont
2-amino-2-methylbutanenitrile	[4475-95-0]	DuPont
2-amino-2,4-dimethylpentane-nitrile	[26842-43-3]	DuPont
1-aminocyclohexanecarbonitrile	[5496-10-6]	DuPont
2,2′-azobis(2-methylpropane-nitrile)	[78-67-1]	DuPont, Wako
2,2′azobis(2-methylbutanenitrile)	[13472-08-7]	DuPont, Wako
2,2′-azobis(dimethylpentanenitrile)	[4419-11-8]	DuPont, Wako
2,2′-azobis(4-methoxy-2,4-dimethylpentanenitrile)	[15545-97-8]	Wako
1,1′-azobis(cyanocyclohexane)	[2094-98-6]	DuPont
benzonitrile	[100-47-0]	PMC
n-butyronitrile	[109-74-0]	Eastman Chemicals
i-butyronitrile	[78-82-0]	Eastman Chemicals
cyanoacetic acid	[372-09-8]	Huls America
-methyl ester	[105-34-0]	Huls America
-ethyl ester	[105-56-6]	Huls America
isophthalonitrile	[626-17-5]	DuPont, Twin Lakes
2-methyl-3-butenenitrile	[16529-56-9]	DuPont
2-methylglutaronitrile	[4553-62-2]	DuPont
2-pentenenitrile	[13284-42-9]	DuPont
3-pentenenitrile	[4635-87-4]	DuPont
propionitrile	[107-12-0]	Monsanto
miscellaneous alkyl and fatty acid nitriles		Akzo Nobel, Dixie, Eneco, Hampshire, Henkel, High Point, Hilton Davis, Olin, Witco[b]

[a]Ref. 11.
[b]*Bought by GNI in 1995.

Table 2. **Some Physical Properties of Acetonitrile**

Property	Value
CAS Registry Number	[75-05-8]
mol wt	41.05
bp (at 101.3 kPa = 1 atm), °C	81.6
freezing pt, °C	−45.7
density (at 20°C), g/cm^3	0.786
n_D^{20}	1.3441
viscosity (at 20°C), mPa·s(=cP)	0.35
heat of vaporization (at 80°C), J/kg[a]	72.7×10^4
heat of fusion (at −45.7°C), J/kg[a]	21.8×10^4
heat of combustion (at 25°C), J/kg[a]	31.03×10^6
heat capacity (liquid at 20°C), J/(kg·K)[a]	22.59×10^2
surface tension, mN/m (dyn/cm)	29.3
coefficient of expansion (at 20°C per °C)	1.37×10^{-3}
specific conductance (at 25°C), S	$(5–9) \times 10^{-8}$
dipole moment, C·m[b]	10.675×10^{-30}
dielectric constant, °C	
at 0	42.0
at 20	38.8
at 81.6	26.2
evaporation rate (butyl acetate = 100)	579
flash pt (COC[c]), °C	6
flammable limits (in air), vol %	
lower	4.4
upper	16.0

[a]To convert J to cal, divide by 4.184.
[b]To convert C·m to D, divide by 3.336×10^{-30}.
[c]COC = Cleveland open cup.

Table 3. **Acetonitrile Binary Azeotropes**[a]

Component	Bp (at 101.3 kPa = 1 atm)	Acetonitrile, wt%
benzene	73	34
carbon tetrachoride	65	17
1,2-dichloroethane	79	79
ethanol	73	44
ethyl acetate	75	23
methanol	63	81
water	77	84

[a]Ref. 14.

Table 4. **Specifications for Commercial Acetonitrile**

Specification	Value
sp gr, at 20°C	0.783–0.787
distillation range, °C	
initial min	80.5
end pt, max	82.5
purity (min), wt%	99.0
acidity (max), wt%	0.05
copper (max), ppm	0.5
iron (max), ppm	0.5
water (max), wt%	0.3
color (max), Pt–Co	15

Table 5. **Some Physical Properties of Adiponitrile**

Property	Value
CAS Registry Number	[111-69-3]
mol wt	108.14
bp, °C	
at 101.7 kPa[a]	295
at 1.3 kPa[a]	154
freezing pt, °C	2.49
density (at 20°C), g/cm^3	0.965
n_D^{20}	1.4343
viscosity, mPa·s (= cP)	
at 20°C	9.1
at 70°C	2.6
heat of vaporization, J/kg[b]	70.4×10^4
heat of fusion (at 1°C), J/kg[b]	21.3×10^4
heat of combustion, J/kg[b]	40.4×10^6
critical temperature, °C	507
critical pressure, MPa[c]	2.8
specific conductance, S	3.5×10^{-8}
flash pt (closed cup), °C	159
autoignition temperature, °C	550
flammable limits (in air), vol %	
lower	1.7
upper	5.0

[a]To convert kPa to mm Hg, multiply by 7.5.
[b]To convert J to cal, divide by 4.184.
[c]To convert MPa to atm, divide by 0.101.

Table 6. **Aminonitrile Shipping Information**

DOT/IMO	AN-64[a]	AN-67[a]	AN-52[a]	AN-88[a]
hazard class	6.1	6.1	6.1	3
subs. hazard class	3	3	3	6.1
UN No.	2929	2929	2929	1992
label	POISON,	FLAMMABLE	LIQUID	
packing group	I	I	II	II

[a]Shipping name: AN-64, Toxic Liquids, Flammable, Organic, N.O.S. (2-amino-2-methylpropanenitrile). AN-67, Toxic Liquids, Flammable, Organic, N.O.S. (2-amino-2-methylbutanenitrile). AN-52, Toxic Liquids, Flammable, Organic, N.O.S. (2-amino-2,4-dimethylpentanenitrile). AN-88, Flammable Liquids, Toxic, N.O.S. (1-amino cyclohexane carbonitrile).

Table 7. **Properties of Azobisnitriles**

Property	V-70[b]	Vazo 52[a] V-65[b]	Vazo 64[a] V-60[b]	Vazo 67[a] V-59[b]	Vazo 88[a]
CAS Registry Number	[15545-97-8]	[4419-11-8]	[78-67-1]	[13472-08-7]	[2094-98-6]
mol wt	308.4	248.4	164.2	192.3	244.3
mp, °C	50–96 d	45–70	100–103	48–52	113–115
specific gravity			1.128		
bulk density, kg/m^3[c]		~450	~265	~450	~425
specific heat, kJ/kg·K[d]		~1.7	~1.7	~1.7	~1.7
heat of combustion, kJ/kg·mol[a]			5.05		
10-h half-life decomp temp, °C[e]	30	52	64	67	88
half-life ($t_{1/2}$), min log ($t_{1/2}$) = A(1/T)–B					
A		6767	7142	7492	7660
B		18.04	18.36	19.22	18.39
max storage temp, °C		10	24	24	35

[a]Registered trademark of DuPont.
[b]Wako name.
[c]In form of white noodles.
[d]To convert J to cal, divide by 4.184.
[e]In toluene.
[f]See text for structures and chemical names.

Table 8. **Azobisnitrile Shipping Information**

DOT/IMO	Vazo 64[a]	Vazo 67[a]	Vazo 52[a]	Vazo 88[a]
hazard class	4.1	4.1	4.1	4.1
UN No.	3234	3236	3236	3226
label	--------	FLAMMABLE	SOLID	--------
packing group	II	II	II	II

[a]Shipping name (see text for structure): Vazo-64, Self-Reactive Solid Type C, Temperature Con-trolled (2,2′-azodi(iso-butyronitrile)). Vazo-67, Self-Reactive Solid Type D, Temperature Controlled (2,2′-azodi(2-methylbutyronitrile)). Vazo-52, Self-Reactive Solid Type D, Temperature Controlled (2,2′-azodi (2,4-dimethylvaleronitrile)). Vazo-88, Self-Reactive Solid Type D (1,1′-azodi (hexahydrobenzonitrile)).

Table 9. **Toxicity of Vazo Compounds**

	Skin				
	Irritant	Sensitive	Mild eye Irritant	Inhalation,[b] mg/m^3	Oral[c], mg/kg
Vazo-64	no	no	yes	950	450
Vazo-67	no	no	no	>8,900	982
Vazo-52	yes	no	yes		>5,000
Vazo-88	no		yes		>11,800

[a]Shipping name (see text for structure): Vazo-64, Self-Reactive Solid Type C, Temperature Con-trolled (2,2′-azodi(iso-butyronitrile)). Vazo-67, Self-Reactive Solid Type D, Temperature Controlled (2,2′-azodi(2-methylbutyronitrile)). Vazo-52, Self-Reactive Solid Type D, Temperature Controlled (2,2′-azodi (2,4-dimethylvaleronitrile)). Vazo-88, Self-Reactive Solid Type D (1,1′-azodi (hexahydrobenzonitrile)).

[b]Vazo-64, ALC (approx lethal concentration); Vazo-67, LC_{50}.

[c]Vazo-64, -52, -88, ALD (approx lethal dose); Vazo-67, LD_{50}.

[d]See text for chemical names and structures.

Table 10. **Some Physical Properties of Benzonitrile**

Property	Value
mol wt	103.12
bp (at 101.3 kPa = 1 atm), °C	191.1
freezing pt, °C	−12.8
density (at 20°C), g/cm^3	1.0102
n_D^{20}	1.5289
viscosity, mPa·s (= cP)	1.24
heat of vaporization, mJ/kg[a]	3.66
surface tension (at 20°C), mN/m (= dyn/cm)	39.0
coefficient of expansion (per °C)	9×10^{-4}
dielectric constant (at 25°C)	25.5
dipole moment (at 22°C), C·m[b]	13.144×10^{-30}
evaporation rate (butyl acetate = 100)	13
flash pt (COC)[C], °C	79

[a]To convert J to cal, divide by 4.184.
[b]To convert C·m to D, divide by 3.336×10^{-30}.
[c]COC = Cleveland open cup.

Table 11. **Some Physical Properties of Cyanoacetic Acid and Methyl and Ethyl Esters**[a]

	Cyanoacetic acid, $NCCH_2COOH$	Methyl ester, $NCCH_2COOCH_3$	Ethyl ester, $NCCH_2COOC_2H_5$
mol wt	85.06	99.09	113.11
bp, °C	108[b]	206	208–210
mp, °C	67		−22.5
n_D^{20}		1.419	1.4177
flash pt, °C	107	110	110

[a]Ref. 74.
[b]At 2 kPa (15 mm Hg).

Table 12. **Some Physical Properties of Methylglutaronitrile**

Property	Values
mol wt	108.14
physical state	colorless liquid
bp, °C (at 101.3 kPa)	274
mp, °C	−44
vapor pressure (kPa at 179°C)	8.1
specific gravity, at 25°C	0.95
flash pt, °C	98
flammable limits (in air), vol %	
lower	0.3
upper	3.25

Table 13. **Some Physical Properties of Pentenenitrile**

Property	3-Pentenenitrile	*cis*-2-Pentenenitrile
mol wt	81.05	81.05
physical state	colorless liquid	colorless liquid
bp, °C	145	127
vapor pressure (kPa at 50°C)	3.3	6.3
specific gravity, at 20°C	0.83	
flash pt, °C	40	26

Table 14. **Some Physical Properties of Fatty Acid Nitriles**

Nitrile	CAS Registry Number	Bp,[a] °C	Freezing pt, °C	Iodine value
oleyl	[112-91-4]	>325	5	85 min
coco	[61789-53-5]			15 max
tallow	[61790-28-1]	330–360	4	44–60
stearyl	[638-65-3]	330–360	39	4 max

[a]At 101.3 kPa.