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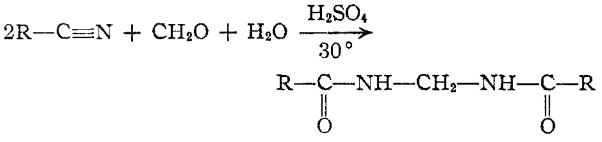
Acid-catalyzed Reactions of Nitriles. I. The Reaction of Nitriles with Formaldehyde[1]

BY EUGENE E. MAGAT, BURT F. FARIS, JOHN E. REITH AND L. FRANK SALISBURY

Nitriles react with formaldehyde in strong sulfuric acid solutions (65 to 100%) at room temperature to give yields of methylene-bis-amides often exceeding 90% in less than one hour. The reaction is applicable to other aldehydes, but yields are markedly reduced. Methylene-bis-amides in sulfuric–formic acid solution undergo amide interchange when nitriles are added to the reaction mixture; the new nitrile appears as a component of the new methylene-bis-amide equilibrium mixture.

In the course of studies dealing with the reaction of benzene derivatives with formaldehyde in 85% sulfuric acid solution to form diphenylmethanes, it was found that *p*-tolunitrile gives none of the expected diphenylmethane derivative but only methylene-bis-*p*-toluamide. A similar reaction of nitriles with formaldehyde was previously reported by Hepp,[2] but no yields were given and the scope and mechanism of the reaction were not examined critically.



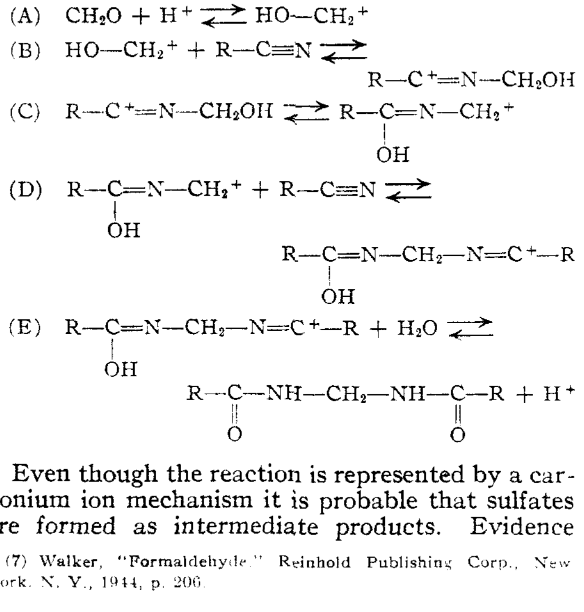
$$2R{-}C{\equiv}N + CH_2O + H_2O \xrightarrow[30°]{H_2SO_4} R{-}\underset{\underset{O}{\|}}{C}{-}NH{-}CH_2{-}NH{-}\underset{\underset{O}{\|}}{C}{-}R$$

This reaction of nitriles and aldehydes which has been used only occasionally since its discovery[3,4,5] has been reinvestigated since it provides a novel method for the preparation of polyamides in acid solution at room temperature. Polyamides derived from the reaction of dinitriles with formaldehyde are described in the following paper of this series.[6]

The reaction of nitriles with formaldehyde is exothermic and occurs at room temperature with remarkable ease to give high yields of methylene-bis-amides (often over 90%). The reaction is effected by adding a mixture of nitrile and formaldehyde (preferably as trioxane which is soluble in most liquid nitriles) to an excess of 85% sulfuric acid solution, keeping the temperature at 30° by cooling. At the completion of the reaction (from 1 to 6 hours), the reaction mixture is poured into an excess of ice and water. The methylene-bis-amides are usually precipitated as water-insoluble solids which may be isolated in a high degree of purity by filtration.

The amidation reaction provides highest yields with formaldehyde but other aldehydes such as acetaldehyde, butyraldehyde and chloral can be used to give compounds of the type R–CO–NH–C(R′)H–NH–CO–R where R′ is CH_3–, C_3H_7–, Cl_3C–. Aldehydes which contain hydrogen atoms on the carbon atom adjacent to the carbonyl group undergo a number of self-condensation reactions under the influence of sulfuric acid, and therefore, give markedly lower yields in the reaction with nitriles. The reaction is general with nitriles and gives derivatives which are normally high melting solids. Of special interest is the reaction of formaldehyde and acrylonitrile which yields methylene-bis-acrylamide, a useful monomer for vinyl polymerization. The methylene-bis-amides prepared in the course of this investigation are reported in Table I. In the early experiments chloroform and cyclohexane were used as solvents for the nitrile–aldehyde mixture. In subsequent preparations the procedure was simplified by adding the mixture or solution of reactants to 85% sulfuric acid which acts both as a catalyst and a solvent. This latter procedure ensures a homogeneous system for the entire course of the reaction and leads to improved yields.

Although it might appear that the reaction involves hydrolysis of the nitrile to an amide with the subsequent reaction of two moles of the amide with one mole of formaldehyde to form a methylene-bis-amide,[7] this is not the case, since (a) amides do not react with formaldehyde under the reaction conditions used for nitriles and (b) nitriles are not converted to amides by 85% sulfuric acid at a rate comparable to the reaction of nitriles with formaldehyde. The reaction of nitriles with formaldehyde appears to proceed by a carbonium ion mechanism and may be represented by the series of equations



$$\text{(A)}\quad CH_2O + H^+ \rightleftarrows HO{-}CH_2^+$$

$$\text{(B)}\quad HO{-}CH_2^+ + R{-}C{\equiv}N \rightleftarrows R{-}C^+{=}N{-}CH_2OH$$

$$\text{(C)}\quad R{-}C^+{=}N{-}CH_2OH \rightleftarrows R{-}\underset{\underset{OH}{|}}{C}{=}N{-}CH_2^+$$

$$\text{(D)}\quad R{-}\underset{\underset{OH}{|}}{C}{=}N{-}CH_2^+ + R{-}C{\equiv}N \rightleftarrows R{-}\underset{\underset{OH}{|}}{C}{=}N{-}CH_2{-}N{=}C^+{-}R$$

$$\text{(E)}\quad R{-}\underset{\underset{OH}{|}}{C}{=}N{-}CH_2{-}N{=}C^+{-}R + H_2O \rightleftarrows R{-}\underset{\underset{O}{\|}}{C}{-}NH{-}CH_2{-}NH{-}\underset{\underset{O}{\|}}{C}{-}R + H^+$$

Even though the reaction is represented by a carbonium ion mechanism it is probable that sulfates are formed as intermediate products. Evidence

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[1] Presented before the Division of Organic Chemistry at the April, 1950, Meeting of the American Chemical Society. After submitting the manuscript to the Journal, it was found that Mowry and Ringwald had submitted a paper on the preparation of polyamides from azelaonitrile and formaldehyde, which deals with the mechanism of the reaction of nitriles with formaldehyde; THIS JOURNAL, **72**, 4439 (1950).

[2] Hepp and Spiess, *Ber.*, **9**, 1424 (1876); Hepp, *ibid.*, **10**, 1649 (1877).

[3] Thiesing, *J. prakt. Chem.*, [2] **44**, 570 (1891).

[4] Batt and Woodcock, *J. Chem. Soc.*, 2322 (1948).

[5] Kraut, *Ann.*, **258**, 109 (1890).

[6] Magat, Chandler, Faris, Reith and Salisbury, THIS JOURNAL, **73**, 1031 (1951).

[7] Walker, "Formaldehyde," Reinhold Publishing Corp., New York, N. Y., 1944, p. 206.

TABLE I

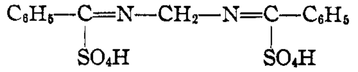
REACTION OF NITRILES WITH ALDEHYDES

$2R—CN + R'—CHO + H_2O \longrightarrow R—CO—NH—CH(R')—NH—CO—R$

Reactants		Solvent	Reacn. time, min.	Product	Yield, %	M.p., °C., uncor.	Nitrogen, %	
Nitrile	Aldehyde						Calcd.	Found
$C_6H_5—CN$	CH_2O	85% H_2SO_4	60	$C_{15}H_{14}O_2N_2$	90	216–218[2]	11.0	11.0
$C_6H_5—CN$	CH_2O	Cyclohexane	45		60	216–218		
p-$CH_3—C_6H_4—CN$	CH_2O	Cyclohexane	45	$C_{17}H_{18}O_2N_2$	32	209–210	10.0	9.8
p-$CH_3—C_6H_4—CN$	CH_2O	85% H_2SO_4	180		83	209–210		
$C_6H_5—CH_2—CN$	CH_2O	Cyclohexane	75	$C_{17}H_{18}O_2N_2$	30	209–211[2]	10.0	10.1
p-$Cl—CH_2—C_6H_4—CN$	CH_2O	Chloroform	75	$C_{17}H_{16}O_2N_2Cl_2$	75	208–210	8.0	7.8
p-$CH_3OOC—C_6H_4—CN$	CH_2O	Chloroform	120	$C_{19}H_{18}O_6N_2$	50	256–258	7.5	7.5
o-$C_6H_4(CN)_2$	CH_2O	Chloroform	75	$C_{17}H_{10}O_4N_2$	20	221–223[a]	9.2	9.1
$C_2H_5OOC—CH_2—CN$	CH_2O	Cyclohexane	75	$C_{11}H_{18}O_6N_2$	5	135–137	10.2	10.5
$CH_2═CH—CN$	CH_2O	85% H_2SO_4	180	$C_7H_{10}O_2N_2$	86	185	18.2	18.2
$CH_2═CH—CH_2—CN$	CH_2O	75% H_2SO_4	120	$C_9H_{14}O_2N_2$	18	......	15.4	15.3
$CH_3—CH═CH—CH_2—CN$	CH_2O	90% H_2SO_4	120	$C_{11}H_{18}O_2N_2$	9	201–204	13.3	13.3
$CH_2═CH—CN$	$CCl_3—CHO$	75% H_2SO_4	120	$C_8H_9N_2O_2Cl_3$	18	......	10.3	8.5[b]
$C_3H_7—CN$	CH_2O	85% H_2SO_4	20	$C_9H_{18}O_2N_2$	40	183–186	15.0	15.0
$C_3H_7—CN$	$C_3H_7—CHO$	96% H_2SO_4	100	$C_{12}H_{24}O_2N_2$	19	132–133	12.2	11.2
$C_3H_7—CN$	$CCl_3—CHO$	96% H_2SO_4	210	$C_{10}H_{17}O_2N_2Cl_3$	67	217–218	9.2	8.7

[a] The reaction product is methylene-bis-phthalimide. [b] The reaction product is a mixture of trichloroethylidene-bis-acrylamide and N-trichloromethylmethylolacrylamide.

for the formation of sulfur-containing compounds has been obtained by effecting the benzonitrile–formaldehyde reaction in an acetic–sulfuric acid mixture and pouring the resulting solution into an excess of acetic acid. Upon standing, a crop of crystals (I) melting at 150–160° was isolated. This compound contained sulfur, but upon recrystallization from water or alcohol only methylene-bis-benzamide melting at 212–216° was found. The filtrate from the recrystallization gave a strong test for sulfate ions. An analysis of the crude intermediate (I) did not correspond in sulfur content with that expected for



$$C_6H_5—\underset{\displaystyle SO_4H}{\underset{|}{C}}═N—CH_2—N═\underset{\displaystyle SO_4H}{\underset{|}{C}}—C_6H_5$$

The reversibility of reactions (D) and (E) has been demonstrated by dissolving methylene-bis-benzamide in an acid solution in the presence of a nitrile containing a chlorine atom and showing that the new reaction product contains chlorine. All traces of chloro-nitrile were removed by recrystallization of the reaction products. The absence of any nitrile group was shown by infrared analysis. Methylene-bis-benzamide was dissolved in a mixture of 90% formic and 96% sulfuric acids (8:3 volume ratio) in the presence of p-chlorobenzonitrile and after 16 hours at 30° the reaction product was precipitated by pouring the reaction mixture into an excess of water. After recrystallization from alcohol, the product showed an 8.5% chlorine content; the theoretical chlorine value for Cl-C_6H_4-CO-NH-CH_2-NH-CO-C_6H_5 is 12.3%. This result corresponds to a 69% interchange between methylene-bis-benzamide and p-chlorobenzonitrile. Using chloroacetonitrile under identical experimental conditions, the final product contained 2.7 and 5.8% chlorine, respectively, for a 1:1 and 2:1 molar ratio of chloroacetonitrile to methylene-bis-benzamide. The calculated chlorine content for Cl-CH_2-CO-NH-CH_2-NH-CO-C_6H_5 is 15.6%; therefore, the interchange occurred to an extent of 17 and 37%, respectively. When these chloronitrile–methylene-bis-amide interchange experiments were carried out in 85 or 96% sulfuric acid alone, the product showed only 0.3–0.5% chlorine indicating no appreciable exchange. The reason why a mixture of sulfuric and formic acids causes interchange whereas sulfuric acid alone does not, is not clearly understood.

Owing to its ionic character, the reaction of nitriles with formaldehyde is influenced greatly by the acid strength of the reaction system. This effect is especially pronounced in the preparation of polyamides from dinitriles and formaldehyde.[6] In general, yields and reaction rates vary widely with the nature of the aldehyde or nitrile used in the reaction.

The concentration of the sulfuric acid needed to effect the reaction is fairly specific for each nitrile–aldehyde system and is in the 65–100% range. The yield of reaction product from benzonitrile and formaldehyde at 30° in aqueous sulfuric acid was nil up to 65% acid concentration and reached a maximum of 91% in 80 to 85% sulfuric acid. When aldehydes other than formaldehyde are used, concentrated sulfuric acid is needed to promote the reaction of the nitrile with the aldehyde to give a methylene-bis-amide. Other acids such as 85% phosphoric acid, methane sulfonic acid and formic acid or mixtures of these acids with sulfuric acid have been used to induce the reaction between nitriles and formaldehyde at room temperature. When formic acid alone is used, higher temperatures are required to bring about the reaction. For example, with benzonitrile and formaldehyde in 90% formic acid, a yield of 22% of methylene-bis-amide was obtained after 5 hours at 101°.

Generally sulfuric acid is used in excess and acts as a solvent. However, no molar excess of sulfuric acid is necessary even though an excess of acid increases the reaction rate. For example, equimolar amounts of 100% sulfuric acid, benzonitrile and formaldehyde in glacial acetic acid as the solvent gave an 81% yield of methylene-bis-benzamide after 72 hours. Even when the sulfuric acid (85%) was used in one-tenth of the theoretical amount in the reaction of butyronitrile and formaldehyde, a 17% yield of methylene-bis-butyramide was obtained in 30 minutes at 30°. When the molar ratio of acid to nitrile is reduced as low as 0.013:1 and the mixture is heated at 80°, the product is a triacyl hexahydro-*s*-triazine as reported by Gradsten and Pollock[8a] and Wegler and Ballauf,[8b] and only negligible amounts of methylene-bis-amides are formed as by-products.

The yields of methylene-bis-benzamide obtained from benzonitrile and formaldehyde are almost quantitative in short periods of time. Using 85% H_2SO_4, the condensation product is formed in 90% yield in 5 minutes at 30°.

The theoretical molar ratio of nitrile to formaldehyde should be 2:1. When a tenfold excess of formaldehyde is used (nitrile/formaldehyde ratio of 2:10) yields of methylene-bis-benzamide are 48% whereas for a ratio of 2:1 the yields are 89%. From a consideration of the reaction mechanism it would be expected that the condensation of a nitrile with a large excess of formaldehyde should stop at the N-methylolamide stage, and thus decrease the yields of the expected bis-amides. No N-methylolbenzamide has been isolated from the interaction of benzonitrile and an excess of formaldehyde but no positive proof for its absence was obtained. Failure to isolate any N-methylolamide as side product may be ascribed to the solubility of this type of compound in acids. Since N-methylolamides might be present in the reaction mixture, it is important to differentiate the two paths by which they may be converted to methylene-bis-amides. The first method is the reaction with a nitrile,[9] whereas the second method is a disproportionation reaction which occurs in the presence of acids.[10]

$$2C_6H_5\text{—CO—NH—}CH_2OH \longrightarrow$$
$$C_6H_5\text{—CO—NH—}CH_2\text{—NH—CO—}C_6H_5 + CH_2O + H_2O$$

Thus if methylolbenzamide is dissolved in concentrated H_2SO_4 for 2 hours and water is then added, a 25% yield of methylene-bis-benzamide is obtained. This disproportionation side reaction is faster with N-methylolamides of aromatic acids than with those derived from aliphatic acids.

Methylene-bis-amides are surprisingly stable compounds considering that they are derived from methylene diamine which is unstable in the free state. The amides melt without decomposition and do not evolve formaldehyde upon heating even above their decomposition temperature. Methylene-bis-benzamide is stable to hot dilute aqueous acids and alkalies (10% concentration), but is hydrolyzed by refluxing with phosphoric acid or alkali in ethylene glycol.

Experimental

The experimental procedure used in most of the acid-catalyzed reactions to be described consists of adding a mixture of aldehyde and nitrile to an acid solution, keeping the reaction temperature at 30° and pouring the reaction mixture into an excess of ice and water to precipitate the methylene-bis-amide reaction product.

Reaction of *p*-Tolunitrile and Formaldehyde.—A solution of trioxane (0.05 mole, 1.5 g.) in *p*-tolunitrile (0.1 mole, 11.7 g.) was added slowly with stirring to an 85% solution of sulfuric acid (38 cc.) in a 125-cc. three-necked flask. The temperature was maintained at 30° by cooling with an ice-bath. After 3 hours the solution was poured into 300 cc. of ice and water. Methylene-bis-*p*-toluamide separated as white crystals which were filtered and recrystallized from 95% alcohol. The yield of product was 12.4 g. (83%), melting at 209–210° (uncor.).

Anal. Calcd. for $C_{17}H_{18}O_2N_2$: C, 72.5; H, 6.4; N, 9.9; mol. wt., 282. Found: C, 72.9; H, 6.5; N, 10.0; mol. wt., 270, 279 (ebullioscopic).

Hydrolysis of 3 g. of the product in a solution of potassium hydroxide (5 g.) in ethylene glycol (50 cc.) and water (1 cc.) at 200° for 2 hours gave upon acidification *p*-toluic acid, m.p. 177° (reported 178°).

When the *p*-tolunitrile was allowed to react with formaldehyde in cyclohexane as a solvent, lower yields were obtained because the reaction product, methylene-bis-*p*-toluamide, was insoluble in cyclohexane and separated out of the reaction mixture as a sticky, oily layer which occluded the small amount of sulfuric acid catalyst.

Formaldehyde Analysis of Methylene-bis-amides.—Formaldehyde was determined from methylene-bis-amides as a measure of their methylenediamine content by heating the amide with 45% phosphoric acid to a reflux and collecting the formaldehyde which distilled into water. The formaldehyde was titrated by the sodium sulfite method.[11] Methylene-bis-butyramide gave the following results.

Anal. Calcd. for $C_9H_{18}O_2N_2$: CH_2O, 16.1. Found: CH_2O, 15.8.

Isolation of a Sulfur-containing Intermediate from the Reaction of Benzonitrile and Formaldehyde.—A solution of trioxane (0.05 mole, 1.5 g.) in benzonitrile (0.1 mole, 10.3 g.) was slowly added to a solution of 100% sulfuric acid (50 cc.) and glacial acetic acid (20 cc.). The temperature was maintained at 30° for 1 hour by cooling and the resulting solution was then poured into 300 cc. of glacial acetic acid. The final solution was left in an evaporating dish for 2 days at 0 to 5°. Two crops of crystals were isolated by filtration to yield 9.95 g. of a white crystalline solid melting at 150–160°. Recrystallization of the solid from water or alcohol yielded a product melting at 208–212° which was found to be identical with methylene-bis-benzamide. Analytical results on crystals isolated from acetic acid were: *Anal.* Calcd. for $C_{15}H_{14}N_2S_2O_3$: C, 43.5; H, 3.4; N, 6.8; S, 15.5; O, 31.0. Found: C, 45.6; H, 4.8; N, 7.0; S, 10.4; O, 32.2 (by difference).

Reaction of Butyronitrile and Butyraldehyde.—A solution of butyronitrile (0.19 mole, 13.0 g.) and butyraldehyde (0.096 mole, 6.6 g.) was added slowly to 96% sulfuric acid (75 cc.) and the solution was kept at 0° for 2 hours. The reaction mixture was poured into water to precipitate butylidene-bis-butyramide. After filtration the product was recrystallized from *n*-heptane to give 4.2 g. (19% yield) of amide derivative melting at 132–133°.

Anal. Calcd. for $C_{12}H_{24}O_2N_2$: C, 63.1; H, 10.6; N, 12.3. Found: C, 64.5; H, 10.7; N, 11.2.

Reaction of Acrylonitrile and Formaldehyde.—In a 500-ml., 3-necked flask equipped with stirrer, thermometer and dropping funnel was placed 150 ml. (2.1 mole) of acrylonitrile (stabilized with copper salts). In a separate vessel sulfuric acid (106 cc.) was added to 50 cc. (0.68 mole) of aqueous 37% formaldehyde, with cooling. The mixture of formaldehyde and sulfuric acid was added at room temperature to the stirred acrylonitrile at the rate of about 60 drops/min. The reaction was exothermic and a temperature of 40–45° was maintained by immersion of the reaction flask in a water-bath. The addition was complete in 1.5 hours and the reaction mixture was stirred an additional 2.5 hours, at which time the temperature had dropped to 30°. The pale pink, slightly viscous reaction product was poured onto 500 g. of ice, and powdered calcium carbonate was added until the solution was neutral. It was necessary to add an additional 500 cc. of ice and water to keep the slurry mobile. The solution was filtered and the calcium sulfate

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[8] (a) Gradsten and Pollock, This Journal, **70**, 3079 (1948); (b) Wegler and Ballauf, *Chem. Ber.*, **81**, 527 (1948).

[9] Magat and Salisbury, This Journal, **73**, 1035 (1951).

[10] Einhorn, *Ann.*, **343**, 207 (1905).

[11] Ref. 7, p. 257.

cake was slurried successively with 600 ml. each of water and ethyl alcohol. The combined filtrate was evaporated at 15 mm. pressure by warming on a water-bath (not above 65°). A white solid remained weighing 90.5 g. (86%) after drying in a vacuum desiccator. The crude methylene-bis-acrylamide was recrystallized from a mixture of 300 cc. of acetone and enough water (about 75 cc.) to dissolve the product in the hot solution. The white solid that separated from the cooled solution weighed 71 g. (67.5% yield of purified material), m.p. 185° with polymerization.

Anal. Calcd. for $C_7H_{10}O_2N_2$: N, 18.2; double bonds, 2.0; mol. wt., 154. Found: N, 18.2; double bonds, 2.0, 1.7 (catalytic hydrogenation); mol. wt., 159, 164 (ebullioscopic).

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Acid-catalyzed Reactions of Nitriles. II. Polyamides from Formaldehyde and Dinitriles

BY EUGENE E. MAGAT, LEONARD B. CHANDLER, BURT F. FARIS, JOHN E. REITH AND L. FRANK SALISBURY[1a,1b]

The reaction of adiponitrile with formaldehyde in strong sulfuric acid solution at room temperature has been studied in detail. Infrared, osmotic pressure, end-group determination and solubility data show that the polymer formed is polymonomethylene adipamide (16 nylon). Infrared determinations of –CN end groups suggest that the polymer is highly branched because of the large excess of –CN ends; however, the hydrogenated polymer shows a disproportionately small number of $-NH_2$ ends which arise from hydrogenation of the nitrile ends. The polymer is unusually sensitive to degradation by acids; in 90% formic acid solution at 30° the molecular weight of the polymer is cut to one-half of its original value in one hour. The polymerization has been extended to dinitriles other than adiponitrile and to aldehydes other than formaldehyde.

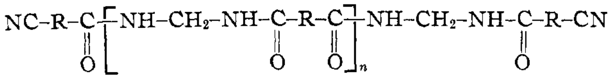
Introduction

In a previous paper[2] it was shown that nitriles react with formaldehyde under the influence of strong sulfuric acid to give methylene-bis-amides

$$2R{-}CN + CH_2O \xrightarrow[H_2O]{H_2SO_4} R{-}CO{-}NH{-}CH_2{-}NH{-}CO{-}R$$

in yields often exceeding 90%. This paper describes work in which the reaction has been extended to the preparation of polyamides from difunctional nitriles and formaldehyde.

$$NC{-}R{-}CN + CH_2O \xrightarrow[H_2O]{H_2SO_4}$$



$$NC{-}R{-}\underset{\underset{O}{\|}}{C}\left[NH{-}CH_2{-}NH{-}\underset{\underset{O}{\|}}{C}{-}R{-}\underset{\underset{O}{\|}}{C}\right]_n NH{-}CH_2{-}NH{-}\underset{\underset{O}{\|}}{C}{-}R{-}CN$$

The reaction product is a polymer which corresponds to the polyamide from monomethylenediamine and the parent acid of the dinitrile.

This new method of obtaining polymers[1b] permits the preparation of a type of polyamide which cannot be obtained by the conventional method of heating a diamine with a dibasic acid since monomethylenediamine is unstable in the free state.[3] Aside from yielding a new polyamide structure, this method differs from the usual procedure for polyamide preparations (heating at 200–300°) in that it is exothermic and proceeds rapidly at room temperature. Good solvents for conducting the polymerization are sulfuric and formic acids or mixtures of the two acids; these acids present the advantage of being solvents for both the starting materials and the polyamide end-product.

The polymerization reaction appears to be general and can be adapted to a large variety of dinitriles. Aldehydes other than formaldehyde can be used in the reaction to yield alkylidene-bis-amide polymers. Most of the work reported here deals with the polymerization of adiponitrile and formaldehyde which leads to polymonomethylene adipamide. In the usual nylon nomenclature the polymer is abbreviated as 16 polyamide where 1 stands for the number of carbon atoms in the diamine and 6 stands for the number of carbon atoms in the dibasic acid.

The technique employed in this type of reaction may be illustrated by the following typical polymer preparation. An equimolar solution (22.5 g.) of adiponitrile and trioxane is added over a period of 5 minutes to a solution of 90% aqueous formic acid (81 cc.) and 96% sulfuric acid (30 cc.). The exothermic reaction is maintained at 30 ± 2° by cooling with an ice-bath. After 20 minutes the initial exothermic character of the reaction subsides and the solution becomes increasingly thicker. Forty-five minutes after the start of the reaction, the product is poured into a Waring Blendor and within 3 to 10 minutes the solution assumes the consistency of a clear thick gel. Water is added immediately with rapid stirring and polymer separates as a white powder. Yields vary with the polymerization conditions and range between 30 and 95%.

The following discussion will deal with (a) the evidence for assigning the 16 polyamide structure to this polymer, (b) the evidence that it is a high molecular weight polymer, (c) the effect of polymerization variables on polymer properties and (d) the reactivity of the polymer chain toward various chemical agents.

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[1] (a) Presented before the Division of Organic Chemistry at the April, 1950, Meeting of the American Chemical Society. (b) Since the manuscript was submitted a paper dealing with the preparation of polyamides from azelaonitrile and formaldehyde has been published, Mowry and Ringwald, THIS JOURNAL, **72**, 4439 (1950). This manuscript was revised to include only new evidence for the structure of the polymers which was not presented by Mowry and Ringwald.

[2] Magat, Faris, Reith and Salisbury, THIS JOURNAL, **73**, 1028 (1951).

[3] Walker, "Formaldehyde," Reinhold Publishing Corp., New York, N. Y., 1944, p. 207.