

in a pressure bottle at 100° for 18 hours. The mixture was allowed to cool, the precipitate filtered, washed with dilute ammonium hydroxide and dried. The product melted at 210°; yield 1.5 g. (18%). The same product was obtained by heating under reflux 5 g. of α -benzamide-4-hydroxycinnamic acid with 5 ml. of pyridine and 20 ml. of water for ten hours. *Anal.* Calcd. for $C_{16}H_{15}O_2N$: C, 75.31; H, 5.43; N, 5.85. Found: C, 75.67; H, 5.30; N, 5.70. On hydrolysis with hydrochloric acid the product gave benzoic acid, ammonium chloride and a gum which could not be purified, apparently a polymer of the unstable and easily resinifiable *p*-hydroxyphenylacetaldehyde. On methylation with dimethyl sulfate a product analyzing correctly for the expected methyl ether was obtained (*Anal.* Calcd. for $C_{16}H_{15}O_2N$: N, 5.54. Found: N, 5.45). This melted at 190–193°, which is appreciably higher than the melting point reported for this compound in the literature (169°).¹⁰ However, discrepancies in the melting points of benzamidostyrenes have been noted by several investigators and the existence of the *cis-trans* isomerism has been suggested.¹¹

α -Benzamido-4-hydroxy-3-methoxystyrene was obtained by heating 32 g. of 3-methoxy-4-hydroxybenzamidocinnamic acid,¹² 32 ml. of concentrated ammonium hydroxide and 10 ml. of water in a pressure bottle for 24 hours at 105°. The product isolated in the usual manner and recrystallized from isopropyl alcohol melted at 173–174°, yield 9 g., 65%. *Anal.* Calcd. for $C_{16}H_{15}O_3N$: C, 71.3; H, 5.57; N, 5.2; mol. wt., 269. Found: C, 71.6; H, 5.30; N, 5.3; mol. wt. (Rast), 262, 265. The hydrolysis with hydrochloric acid gave benzoic acid, am-

monium chloride and a gum having a weak vanillin odor. Methylation with dimethyl sulfate gave a product melting at 137–138°, whose analysis corresponded to that of the expected methyl derivative (*Anal.* Calcd. for $C_{17}H_{17}O_3N$: N, 4.9; Found: N, 5.0). The melting point reported in the literature for this compound is 138°.¹¹ However, on recrystallization from dilute acetic acid the melting point rose to 150–151° while the analytical value did not change.

2-Phenyl-4-(3,4-dimethoxybenzal)-imidazolone-5.—Sixteen grams of the azlactone from veratraldehyde, 5.5 g. of sodium carbonate, 16 ml. of ammonium hydroxide and 30 ml. of water was heated in a pressure bottle for thirty hours at 110–120°. The mixture was allowed to cool, the crystals filtered, washed with dilute ammonium hydroxide and dried. The product melted at 265–266°, yield 12.5 g. (78%). The melting point did not change on recrystallization from acetic acid. *Anal.* Calcd. for $C_{18}H_{16}O_5N_2$: N, 9.1. Found: N, 9.0. 2-Phenyl-4-(3-methoxy-4-ethoxy-benzal)-imidazolone-5 was prepared in the same manner with a yield of 81% and had a melting point of 260–262°.

Summary

Alkoxy and methylenedioxy substituted α -(*N*-acylamido)-cinnamic, phenylpyruvic and phenylthiopyruvic acids react with ammonium hydroxide to yield *N*-phenylacetyl-phenylalanines. Para-substituted acids, under the same conditions, give acylamidostyrenes. An improved procedure for the synthesis of azlactones and 2-phenyl-4-benzalimidazolones-5 is described.

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(10) Rosenmund, Nothnagel and Riesenfeldt, *Ber.*, **60**, 392 (1927).

(11) Sugawara, *J. Pharm. Soc. Japan*, **55**, 58 (1935).

(12) Harrington and McCartney, *Biochem. J.*, **21**, 854 (1927).

[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORIES, MONSANTO CHEMICAL COMPANY]

Polyamides from Azelaonitrile and Formaldehyde

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The normal addition of alcohols or their derivatives to nitriles under acidic conditions leads to the formation of iminoester salts or esters. Certain secondary and tertiary alcohols or related olefins, however, add abnormally to give *N*-substituted amides.¹ Recently Buc² has shown that *N*-methylolamides reacted with nitriles in a similar abnormal fashion to give amides of methylene diamine. A related reaction of two moles of an aromatic nitrile with one of formaldehyde to give methylene bisamides in the presence of excess mineral acids has been known for many years.³

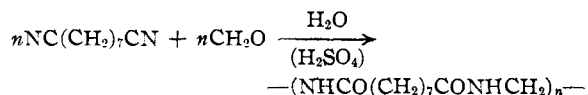
A preliminary extension of this reaction to aliphatic mononitriles indicated that the reaction was rapid and essentially quantitative. Studies

(1) Wieland and Dorner, *Ber.*, **63**, 404 (1930), obtained *N*-cyclohexylformamide from cyclohexene and hydrogen cyanide in the presence of aluminum chloride. See also Ritter, Minieri and Kalish, *THIS JOURNAL*, **70**, 4045, 4048 (1948); Benson and Ritter, *ibid.*, **71**, 4128 (1949). The products obtained from cyclohexanone and nitriles by Bruson, Riener and Riener, *ibid.*, **70**, 483 (1948), are probably better formulated as *N*-substituted amides rather than as iminoesters.

(2) Buc, *THIS JOURNAL*, **69**, 254 (1947).

(3) Hepp and Spiess, *Ber.*, **9**, 1424 (1876); **10**, 1649 (1877); Kraut, *Ann.*, **258**, 109 (1890); Thiesing, *J. prakt. Chem.*, [2] **44**, 570 (1891); Duden and Scharff, *Ann.*, **288**, 247 (1895); Riedel, *J. prakt. Chem.*, [2] **54**, 533 (1896).

were then initiated in an effort to produce polyamides of high molecular weight from a number of aliphatic dinitriles from three to ten carbon atoms. The formaldehyde-azelaonitrile reaction was selected for detailed study since the thermal (m. p. 245–250°) and solubility (soluble only in phenols and formic acid) characteristics of the resultant polymethylene azelamide approximated those of commercial polyhexamethylene adipamide. As

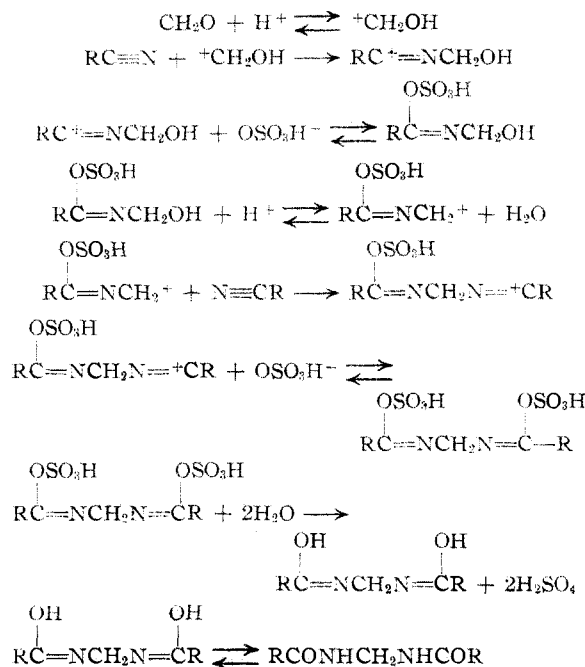


expected, methylene polyamides having a lower carbon to nitrogen ratio, prepared from lower straight chain aliphatic dinitriles, melted at higher temperatures and were less soluble. After a systematic study of reaction variables it was possible to prepare polymethylene azelamide having specific viscosities of 0.9 to 1.2 for a 1% solution in 90% phenol. These values are comparable to those found for samples of commercial flake Nylon which have been shown to have molecular weights of approximately ten thousand.⁴

(4) Taylor, *THIS JOURNAL*, **69**, 635 (1949).

The present polymers are best prepared by reaction of molar quantities of azelaonitrile and formaldehyde (trioxane) with four moles of concentrated sulfuric acid in formic acid solutions at 25–30° for four hours. The viscous solution of the polyamide was then precipitated by quenching in ice-water. Low viscosity (>0.3) samples of polymethylene azelamide precipitated from a formic acid solution of the reaction mixture as a friable powder, while the higher viscosity materials precipitated as tough fibrous particles. The latter could be easily drawn into fibers from a fresh melt on a hot-plate. The polymer treated in this manner, however, was brittle and no longer soluble in phenols, indicative of cross-linking caused by thermal instability in the molten state.

In the presence of sulfuric acid the principal reaction possibly proceeds through the following mechanism⁵:



Several observations indicated that the amide was probably not involved as an intermediate in this reaction. Although appreciable amounts of water may have been present in the sulfuric acid-formic acid solution, the reaction proceeded under strictly anhydrous conditions, for example, with acetic anhydride solvent and boron fluoride catalyst. Moreover, in the sulfuric acid-formic acid system in the absence of formaldehyde, very little, if any, azelamide was formed and most of the nitrile was recovered unchanged after the usual reaction cycle. Although monoamides were coupled by formaldehyde in relatively high yield in dilute aqueous acid solutions, attempts to prepare polymers from adipamide or azelamide failed to give

(5) Price, "Reactions at Carbon-Carbon Double Bonds," Interscience Publishers, New York, N. Y., 1946, pp. 44–46, discusses similar acid-catalyzed reactions of formaldehyde.

products having a specific viscosity (1% in phenol) of over 0.06 either in dilute aqueous acid or under conditions which were optimal for the dinitrile condensation.

A number of reaction variables were studied. The effect of reaction time on the yield and specific viscosity of alcohol-extracted polymer is given in Table I in the experimental part. Maximum conversion and viscosity were observed at 4.5 hours. After this point was reached a chain degradation reaction became predominant, presumably caused by hydrolytic cleavage of the amide linkages. Similar degradation of polymethylene azelamide and to a lesser extent of polyhexamethylene adipamide was observed in formic acid solutions even in the absence of sulfuric acid.⁶

If the ratio of formaldehyde to azelaonitrile appreciably exceeded unity or if insufficient solvent were present, the reaction solution gelled and the polymer after precipitation and washing was insoluble in phenol. Presumably this gelation was caused by a side-reaction involving formation of a reticulated or cross-linked polymer which arose either through simple methylene bridges between amide nitrogens in adjacent chains or through the formation of trifunctional hexahydro-*s*-triazine units. The formation of compounds of the latter type from mononitriles and excess formaldehyde in the presence of catalytic amounts of strong acids has been demonstrated by several workers recently.^{7,8,9}

Substitution of increasing quantities of a chain terminating reagent, caprylonitrile, for equivalent amounts of azelaonitrile caused an expected decrease in the molecular weight of the polymer. However, the melting points and thermal stability of the polymers were not appreciably affected by this modification.

Experimental Part¹⁰

Azelaonitrile.—In a five-liter three-necked flask equipped with a mechanical stirrer, a Dean and Stark trap surmounted by a reflux condenser, gas inlet tube and thermometer was placed 2000 g. of technical azelaic acid and 20 g. of tetraphosphoric acid. The flask was heated to 150° and a brisk stream of gaseous ammonia was passed into the molten acid with stirring. The temperature was then raised to 270° for eight hours during which time 840 ml. of aqueous ammonia solution was drawn off through the trap. The residue was then distilled through a three-foot Vigreux column to give 1255 g. (78%) of crude azelaonitrile, b. p. 150–165° (3 mm.). Refractionation gave purer material, b. p. 159–160° (3 mm.), n_D^{20} 1.4426.¹¹

Polymethylene Azelamide.—A typical polymerization of azelaonitrile and formaldehyde was carried out as follows: In a one-liter three-necked flask equipped with a

(6) See also Korshak, *et al.*, *Acta Physicochim. U.R.S.S.*, **21**, no. 4, 723–740 (1946).

(7) Gradsten and Pollock, *THIS JOURNAL*, **70**, 3079 (1948).

(8) Wegler and Ballauf, *Chem. Ber.*, **81**, 527 (1948).

(9) Gresham and Steadman, *THIS JOURNAL*, **71**, 1872 (1949).

(10) The authors are indebted to John C. Lorenz and Lowell Erbaugh for assistance in part of the experimental work.

(11) von Braun and Danziger, *Ber.*, **45**, 1971 (1912), report b. p. 183° (11 mm.) for a preparation from heptamethylene dibromide.

stirrer, gas-inlet tube and dropping funnel were placed 75.0 g. (0.50 mole) of azelaonitrile, 15.4 g. (0.171 mole) of trioxane (α -trioxymethylene) and 600 ml. of 98% formic acid. The solution was cooled to 5° and 200 g. (2.0 moles) of concentrated sulfuric acid was added with stirring and cooling during fifteen minutes. The solution was then stirred for 3.5 hours at 26–28°. The thick sirup was then rapidly quenched by pouring into 4 liters of well-stirred ice-water. The white polymeric powder which precipitated was filtered, washed successively with water, dilute sodium carbonate solution, water and ethanol. After drying in a vacuum oven at 70° there was obtained 91 g. (92% yield) of white powder, m. p. 240–242°. It was soluble in phenol, cresol and formic acid, but insoluble in other common organic solvents. The specific viscosity of a 1% solution in 90% phenol was 0.91.

Anal. Calcd. for $(C_{10}H_{18}O_2N_2)_x$: C, 60.7; H, 9.15; N, 14.1. Found: C, 59.9; H, 8.66; N, 14.10.

The effect of reaction time on the per cent. conversion to alcohol insoluble polymer and the viscosity of polymer was determined by withdrawing and quenching 25-ml. aliquot samples from the solution after addition of the sulfuric acid was complete. The 0.25 mole run illustrated in Table I was made using the same ratios of reagents as that given above.

TABLE I

Time, hr.	Conversion, %	Specific viscosity (1% in 90% phenol)
0.50	61.5	0.06
1.00	73.4	0.08
2.00	83.5	0.22
3.00	88.0	0.51
4.00	91.0	1.20
5.00	94.0	1.05
6.25	98.3	0.66
7.25	99.7	0.60
8.25	95.5	0.36
27.0	87.5	0.22

The effect of catalyst concentration was determined by following the course of similar runs in which the molar ratio of sulfuric acid to azelaonitrile was varied. The maximum viscosities occurred at the times illustrated in Table II.

TABLE II

Molar ratio (H_2SO_4 /azelaonitrile)	Time, hr.	Specific viscosity (1% in 90% phenol)
2.12	10	0.39
3.00	8	0.82
4.00	4	1.20
5.00	4	0.85

Further increase of the sulfate ion concentration without increasing the sulfuric acid concentration was not beneficial. In a run using four moles of sulfuric acid and two moles of sodium sulfate to one of dinitrile, the maximum specific viscosity observed was 0.26 in 4.5 hours (85% conversion).

Formic acid appeared to be the most satisfactory solvent of those investigated. Low molecular weight polymers were precipitated during the reaction when solvents such

as acetic acid and dioxane were used. Better polymer formation was observed in acetic anhydride, chloroacetic acid, and 85% phosphoric acid. In the latter case polyamide formation occurred in the absence of sulfuric acid. Substantial decreases in the amount of formic acid solvent over that given in the initial example increased the tendency for the reaction to gel. Increasing the amount of solvent merely decreased the rate of reaction. Raising the formaldehyde-azelaonitrile ratio higher than unity also caused more rapid gelation. These factors are illustrated in Table III in which 0.25 mole of azelaonitrile and 0.53 mole of sulfuric acid were treated at 30° for four hours with varying amounts of formaldehyde and formic acid.

TABLE III

Reagent ratio [HCHO/ NC(CH ₂) ₇ CN]	Formic acid, ml.	Gelation time, hr.	Specific viscosity (1% in 90% phenol)
0.984	100	2.5	Insol.
0.984	200	None	0.23
1.012	200	None	0.81
1.024	200	4.0	Insol.
1.024	300	None	0.39
1.024	500	None	0.11
1.039	200	1.5	Insol.

Four-hour conversions of 73 to 86% were observed by the use of several catalysts other than sulfuric acid. These included phosphoric acid, dry hydrogen chloride, boron fluoride-ethyl ether complex, toluenesulfonic acid and ethyl sulfuric acid. These products had specific viscosities of 0.10 to 0.28.

The effect of chain terminating agents on the molecular weight of the polyamides was illustrated by partial substitution of azelaonitrile by equivalent amounts of caprylonitrile. Table IV illustrates one mole runs made at 26–28° for 3.67 hours in the presence of four moles of sulfuric acid in 800 ml. of formic acid. Conversions in all cases were in excess of 96%.

TABLE IV

Azelaonitrile, mole	Caprylonitrile, mole	Specific viscosity (1% in 90% phenol)	M. p., °C.
1.00	0	1.10	242
0.99	0.02	0.39	242
.98	.04	.30	239
.90	.20	.21	239
.80	.40	.13	237
.70	.60	.09	233

Summary

The acid-catalyzed formation of polyamides from dinitriles and formaldehyde has been demonstrated. The conversion of azelaonitrile to polymethylene azelamide has been studied in detail with emphasis on the effect of various reaction variables on the molecular weight of the polyamide.

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