9-Aminononanamide and Nylon-9 From Azelaaldehydic Derivatives of Soybean Oil[1]

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Abstract

9-Aminononanamide, a potential intermediate for nylon-9, was prepared from soybean oil via alkyl soyate, aldehyde oil or soybean amides. All three routes involved various sequences for reductive ozonolysis, reductive amination and ammonolysis. The preferred route is through the alkyl soyates, although the other two have fewer steps. The amino amide is a water-soluble, strongly basic solid that rapidly absorbs atmospheric carbon dioxide and is readily hydrolyzed to 9-aminononanoic acid. Although the amino amide is selfpolymerizable in limited degree, the preferred monomer for nylon-9 is the amino acid. Other new compounds prepared and characterized include azelaaldehydamide, bis(8-carbamoyloctyl)amine; N-(8-carbamoyloctyl)-8-methoxycarbonyloctylamine; 9-hydroxynonanamide; and dimers of the amino amide and the amino ester.

Introduction

Nylons (linear polyamides) have several physical properties in a unique combination that has made them widely useful as both engineering materials and fibers. The large-volume nylons (nylon-6 and -6,6), although desirable because of their high melting points, present some problems in dimensional, electrical and strength uniformity at varying moisture levels. Of the new specialty nylons having high methylene to amide ratios, nylon-9 has perhaps the optimum combination of low water absorption and high melting point (205 C) (1–3). Interest in these higher nylons is growing also because of their greater melt stability and ease of fabrication (1).

Nylon-9 was first described in 1937 by Carothers (4), who emphasized the constant tenacity of its fibers in both the dry and wet state. Details of its synthesis from sebacic acid were later published by other Du Pont investigators (5). Japanese workers have prepared it from oleic acid derived from sperm oil (6,7) and studied the kinetics of polymerization of the monomer, 9-aminononanoic acid (8). One of the current research projects at the Northern Laboratory is the development of an economical synthesis of nylon-9 from soybean oil (9). Soybean oil is a preferred starting material because of its low cost, availability, and high proportion (85%) of unsaturated fatty acids having the first double bond at C_9. Theoretically, 100 lb. of soybean oil would produce 49 lb. of nylon-9. This paper describes exploratory studies on the preparation and polymerization of 9-aminononanamide (Fig. 1, IV), a new compound (10,11).

Experimental Procedures

Materials

Methyl azelaaldehydate (MAZ; III, $R' = CH_3$), $n_D^{20} = 1.4391$, was prepared in 99+% purity from soybean methyl esters via the procedure of Moore et al. (12), and soybean aldehyde oil by the method of Pryde et al. (13). Methyl 9-aminononanoate, $n_D^{30} = 1.4428$, was made from MAZ by a modification of the procedure of Anders et al. (14); methanol was used as the solvent at 60 C and 1000 psi. Soybean and olive amides were prepared by ammonolysis of the appropriate seed oil (Kohlhase et al., unpublished work).

Analytical Methods

Melting points determined at 1–2 C/min on a Kofler hot-stage microscope are uncorrected. Differential thermal analyses (DTA) were run on a Du Pont Model 900 unit, generally at 10 C/min; endotherm "peak" temperatures only are reported, unless noted otherwise, and have ±2 C reproducibility.

Aldehyde titer was determined by back titration of HCl released by reaction between the aldehyde and at least a 10-fold excess of $NH_2OH \cdot HCl$ at 20–25 C for 4–24 hr or under reflux for 30 min.

Amino amide was separated from amino acid and other products on ion-exchange resins; thin layer chromatography and gas liquid chromatography (Kohlhase et al., unpublished work) were used for some analytical separations.

Azelaaldehydamide (I) and Derivatives

Both soybean and olive amides were used as starting materials. For example, a solution of 26.95 g olive amides (0.084 mole unsaturates, mp 73–75.5 C, DTA 76 C, IV 83, 5.1% N), 103.4 g CH_3COOH (1.72

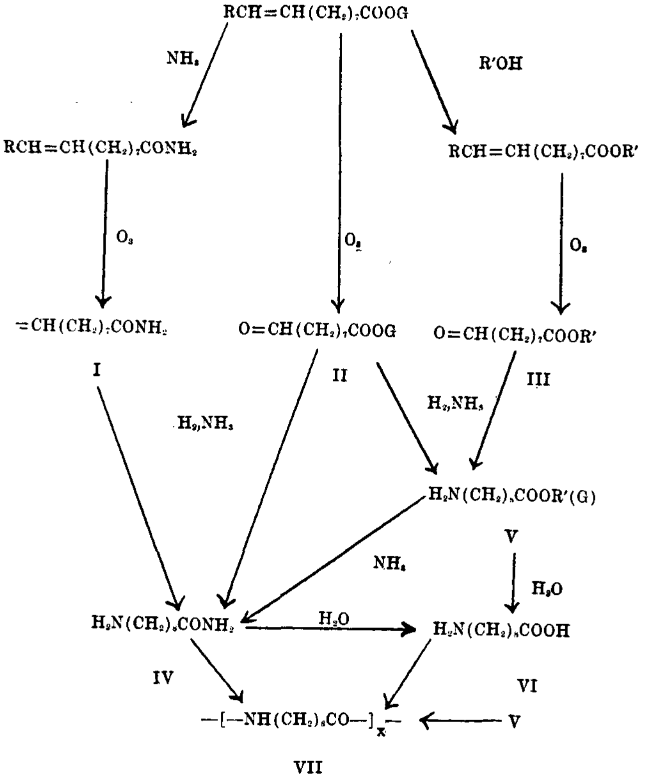

FIG. 1. Routes to 9-aminononanamide (IV) and nylon-9 (VII) from soybean oil.

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moles), and 127.4 g n-C_4H_9OH (1.72 moles) (12) was ozonized at 5 C for 57 min. The mixture was hydrogenated at 7 C until free of peroxides (3.4 g 5% Pd/C, 40 min), warmed to 50 C to dissolve all amides, filtered, cooled to −22 C, and again filtered to remove saturated amides (mp 98–100 C, 4.3 g, 90% theory). The 400 ml filtrate was evaporated at 45 C/0.05 mm to leave 25.9 viscous oil ($n_D^{30} = 1.4517$, 0.0395 mole azelaaldehydamide, 46% of theory as isolated oxime) that was stored in 100 ml CH_3OH under N_2 at −22 C (1.5 g insolubles removed) as solution A. Aldehyde amide was purified by evaporating 9.3 ml solution A at 35 C/0.03 mm and extracting the residue with 80 ml hot heptane, 100 ml ether, and 60 ml CH_2Cl_2. The 0.5 g residue was dissolved in CH_3OH and reprecipitated with CH_2Cl_2 twice to give a soft solid (mp 50–75 C); analysis indicated it to be about 90% pure I. Further purification was not attempted because of its unstable and intractable nature.

Azelaaldehydamide oxime (X) was prepared from a portion of solution A. The crude product (mp 115–123 C) was recrystallized once from H_2O to give pure oxime (Table I). An oxime fraction, believed to be a single geometric isomer (mp 131–132 C, DTA 138 C), was obtained as the first crop (from $CH_3OH/(C_2H_5)_2O$, from another ozonolysis and large-scale oximation.

Azelaaldehydamide semicarbazone (XI) was prepared from another portion of solution A; fatty amides and pelargonaldehyde semicarbazone precipitated first when the reaction mixture was diluted with H_2O and cooled. The combined third and fourth crops were recrystallized from CH_3OH to give pure XI (Table I).

9-Aminononanamide (IV)

From Crude Azelaaldehydamide (I). A solution of 28.2 g crude I (0.0327 mole derived from soybean amides) in 18.6 g 1-propanol, 1.2 g washed Raney nickel, and 50 ml (2.4 moles) liquid NH_3 were charged to a cold 300 ml rocker autoclave. Reaction with H_2 was carried out by pressurizing cold to 500 psi and heating first at 50 C/1500 psi for 2 hr (95 psi ΔP) and then at 90 C/3000 psi (no ΔP) for 1.5 hr. The product (27.9 g green paste) was extracted with 200 ml H_2O, and the extract evaporated to leave 8.51 g ivory-white waxy solid, mp 70–117 C (11.5% N, 6.04 g amino amide). An additional 2.56 g wet solid (mp 70–106 C) obtained from the crude product with 250 ml hot H_2O was fractionated with acetone; the soluble part formed 1.0 g XV (mp 105–122 C, 0.66 g amino amide). The insoluble part was recrystallized from H_2O/acetone to give 1.45 g solid (mp 118–134 C) that analyzed approximately as a 1:1 salt of the amino amide (0.69 g) and azelaamic acid.

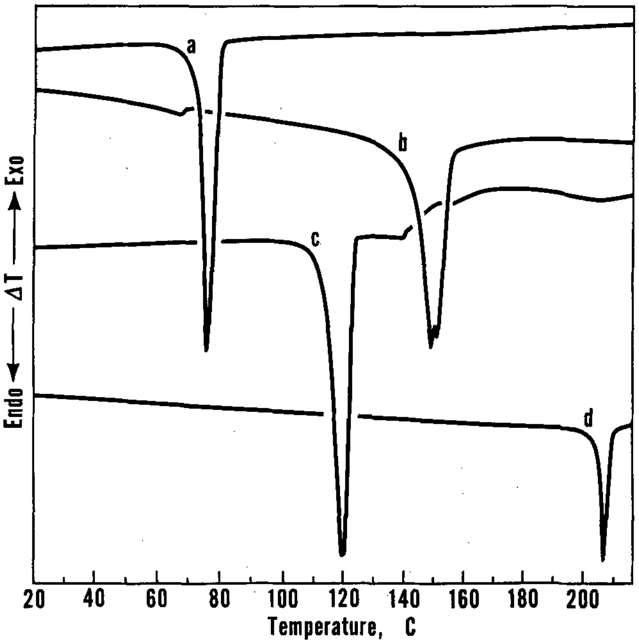

FIG. 2. Differential thermograms of (a) 9-aminononanamide; (b) its carbamate salt; (c) monooxalate; and (d) hemioxalate.

The main 8.51 g H_2O-soluble product was extracted with 200 ml acetone; the extract formed 2.53 g monooxalate (mp 111–120 C, 1.66 g amino amide). The 3.34 g acetone-insoluble solid (mp 119–130 C, from H_2O/acetone) was evidently the azelaamic acid salt of 1.60 g amino amide. The 4.6 g total amino amide was an 82% conversion on aldehyde amide, or 38% on soybean oil unsaturates.

Other Methods. The amino amide was also prepared from glyceryl azelaaldehydate (II) in soybean aldehyde oil, from methyl 9-aminononanoate (V, $R' = CH_3$; monooxalate, XXV), and from MAZ (III, $R' = CH_3$). Ion exchange was used to isolate amino amide in some of this work (Kohlhase et al., unpublished work).

Simultaneous reductive amination and ammonolysis of aldehyde oil gave the amino amide in 56% conversion. The mixture of 10.0 g oil (13) (0.0303 equiv. -CHO), 0.6 g Raney nickel, 50 ml absolute C_2H_5OH, 40 ml n-C_7H_{16}, and 50 ml anhydrous liquid NH_3 was heated with H_2 at 70 C/1500 psi for 1.5 hr and again at 125 C/2000 psi for 3.3 hr.

A 35% yield of amino amide was isolated from ammonolysis of the amino ester in NH_3/CH_3OH at 125–140 C for 5.5 hr. The freshly distilled amino ester was stored in cold NH_3/CH_3OH before the reaction to inhibit poly-condensation.

The MAZ route produced amino amide in 56% yield. The mixture of 5.0 g MAZ (0.0268 mole), 1.16 g 9-aminononanoic acid (0.0067 mole) (3) as ammonolysis catalyst, 0.7 g Raney nickel, 40 ml CH_3OH, and 80 ml anhydrous liquid NH_3 was heated with H_2 at 70 C/1500 psi for 2 hr and at 125 C/2150 psi for 3.5 hr.

Properties. The amino amide was stable for at least one year when stored at 25 C in a closed vial to protect it from atmospheric CO_2; the DTA endotherm (74 C, Fig. 2) was unchanged. Hot-stage melting points were anomalous, presumably due to CO_2 pickup from the air; this sample sintered at 60–80 C and melted at 105–130 C. When heated at 90–95 C for 17 hr under N_2 or in vacuo at 0.02–0.1 mm, there was no appreciable change in the CHN analysis or DTA endotherm (72 C). About half the vacuum-heated sample sublimed, the sublimate analysis and DTA (74 and 149 C) corresponding to a mixture of amino amide and a minor amount of its carbamate (XII, Table I). The infrared spectra of the solid and molten amino amide were different (Fig. 3); care had to be taken in preparing the KBr pellets to minimize CO_2 absorption.

Prolonged contact with acetone illustrated the strongly basic character of IV; it combined with and caused self-condensation of the acetone to mesityl oxide and higher products. Preliminary titration data indicated that K_b for the amino amide is of the order of $1\text{–}2.5 \times 10^{-4}$.

The water solubility of the amino amide rose

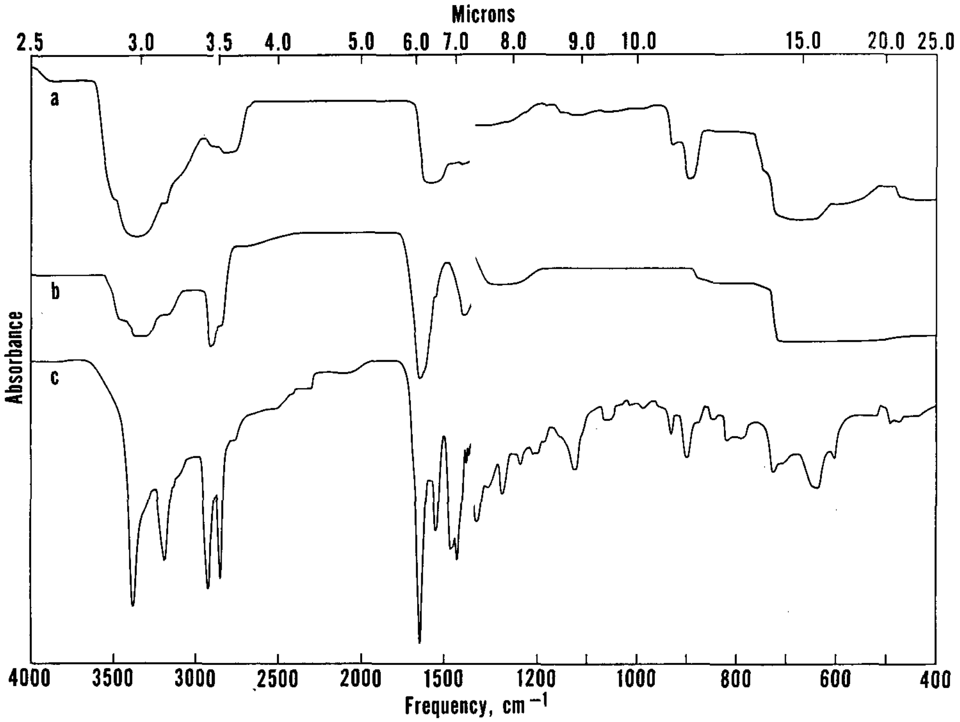

FIG. 3. Infrared spectra of 9-aminononanamide: (a) below the melting point (at 31 C), 0.1% in KBr; (b) same 0.1% sample above the melting point (at 91 C); and (c) at 30 C, 1% in KBr.

sharply with temperature, in contrast to that of the amino acid (Fig. 4), permitting purification of the amino acid by fractional crystallization. Organic solvents provided a sharper solubility difference. The amino amide was very soluble in lower alcohols, moderately in acetone (slow reaction), slightly in benzene, and insoluble in heptane; the amino acid was totally insoluble in the last three. Attempts to purify the amino amide with organic solvents met with little success.

9-Aminononanamide Salts

The carbamate salt (IR, Fig. 5) was readily formed by reaction with atmospheric CO_2; occasional grinding in an agate mortar ensured complete reaction.

Both a hemioxalate (XIV) and a monooxalate salt (XV) were prepared from the amino amide, depending upon the reactant ratios and combining order; partial conversion of the 1:1 salt to the 2:1 salt occurred during extensive recrystallization. Neither salt had a sharp melting point; see Figure 2 for DTAs and Table I for properties. Their infrared spectra were somewhat similar to that of the amino amide, with broader and stronger absorption in the 2700–3300 cm^{-1} region (NH and OH) and near 1600 cm^{-1} ($C = O$). New bands appeared in the spectra of both salts at 1190, 1095, 970, 870, 750 and 450 cm^{-1}; XV at 775 and 490 cm^{-1}; and the XIV hydrate at 570 cm^{-1}. Pure XV precipitated nearly quantitatively when a 0.3–0.5% solution of the amino amide in acetone was added to a slight excess of 1–2% $C_2H_4O_2 \cdot 2H_2O$ in acetone.

The hemioxalate hydrate (0.185 g) was formed when a solution of 0.063 g $C_2H_4O_2 \cdot 2H_2O$ in 10 ml acetone was added to 0.172 g 90% pure amino amide in 100 ml acetone, cooled to 0 C, filtered, and washed. Recrystallization of 0.170 g from 5 ml H_2O (0.013 g insoluble) and 20 ml acetone cooled to 0 C yielded 0.100 g monohydrate. The anhydrous hemioxalate was made by vacuum drying this hydrate at 45 C/0.06 mm.

Other related amino compounds, such as methyl 9-aminononanoate, also readily formed oxalates in a similar manner (Table I).

9-Aminononanamide acetate (XVI) was the product usually isolated from syntheses of the amino amide with CH_3COONH_4 as an ammonolysis catalyst. Thus, the H_2O-soluble product from one MAZ run was recrystallized from ethanol-benzene-heptane to give a mixture of solids that sublimed at 80 C/0.02 mm to produce pure monoacetate.

Other Derivatives

9-Acetamidononanamide (XVII) was prepared by warming 0.359 g amino amide with excess acetic anhydride (8.66 g) at 90 C for 5 min. The mixture was diluted with 11 ml H_2O and evaporated. The product (0.451 g, 100% yield) was recrystallized from 8 ml CH_3OH and 15 ml H_2O (to −22 C) in 80% recovery (IR, Fig. 5).

9-Hydroxynonanamide (XVIII) was prepared by heating a solution of 1.8 g methyl 9-hydroxynonanoate (0.009 mole, 94% pure) (15), 0.74 g CH_3COONH_4, and 40.8 g anhydrous NH_3 in 50 ml CH_3OH in a 300 ml rocker autoclave at 125 C for 6 hr. The H_2O-washed product was purified by dissolving in 40 ml 2.5/1 H_2O/CH_3OH, extracting with 3 × 25 ml benzene to remove unchanged hydroxy ester, evaporating, recrystallizing the 0.87 g residue from 40 ml H_2O, and decolorizing in 80 ml warm H_2O with activated charcoal to give 0.53 g pure XVIII (Table I). The total product in all fractions was about 1.32 g, 85% conversion.

Bis(8-carbamoyloctyl)amine (XIX) was prepared from bis(8-methoxycarbonyloctyl)amine (2.01 g, 0.0056 mole, mp 44–47.5 C) (16), 85 ml CH_3OH, and 16 g anhydrous NH_3, kept at 22 C for 90 hr, heated 8 hr at 50 C, and evaporated on a steam bath for 4 hr. Extraction of the product with 40 ml H_2O removed 0.19 g mixture including some amide acid. Recrystallization of the H_2O-insolubles from 42 ml CH_3OH and 23 ml H_2O (to −22 C) gave 0.77 g impure un-

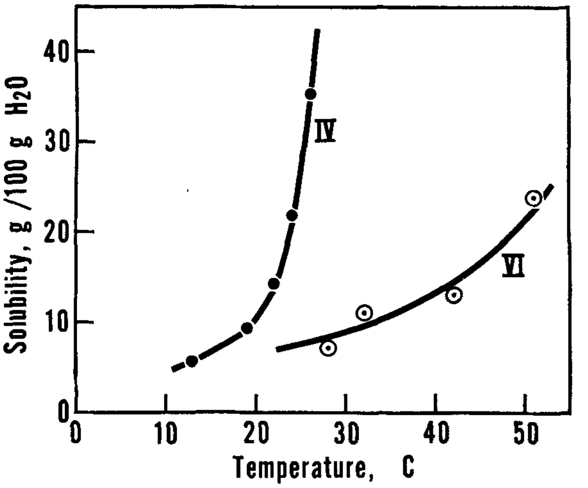

FIG. 4. Water solubility of 9-aminononanamide (IV) and 9-aminononanoic acid (VI).

changed diester (monooxalate mp 110–175 C). The filtrate evaporation residue was extracted with 40 ml hot benzene and with 16 ml H_2O to leave 0.15 g XIX (Table I).

9-(8-Methoxycarbonyloctylamino)nonanamide(XX) was precipitated from the 40 ml benzene extract described above for XIX by slow dilution with 50 ml *n*-heptane and cooling to −22 C. The 0.48 g crude amide ester (mp 80–92 C) was recrystallized from CH_3OH/H_2O (to −22 C).

Oligomeric Products

Methyl 9-(9-aminononanamido)nonanoate (amino ester dimer, VIII) carbamate salt (XXI) was isolated as a by-product of an amino amide synthesis from MAZ that gave amino ester and amino amide in a 2:1 mole ratio. The initially ether-soluble product (primarily a mixture of amino ester and amino amide) became largely ether-insoluble after two days at 25 C. The H_2O-insoluble fraction (mp 84–133 C) was recrystallized from 1:1 *n*-C_3H_7OH:H_2O to give VIII as the carbamate (XXI) (2 dimer · CO_2) containing a small amount of amino amide dimer (IX) (Table I).

9-(9-Aminononanamido)nonanamide (amino amide dimer, IX) carbamate salt (XXII) was obtained when the initially ether-insoluble product (mp 94–106 C) from the same MAZ run was dissolved in CH_3OH and partially (42%) reprecipitated with ether. This precipitate (1.50 g) was extracted with 100 ml hot H_2O (0.51 g insoluble Ni^{+2} complexes), and the extract was cooled to precipitate 0.49 g crude dimer; recrystallization from H_2O gave XXII having the correct analysis (Table I).

9-(9-Aminononanamido)nonanamide (amino amide dimer, IX) diacetate (XXIII) was obtained from XXII by dissolving in excess glacial CH_3COOH and freeze-drying.

9-(9-Acetamidononanamido)nonanamide (XXIV) was prepared from XXII by heating with excess acetic anhydride at 85 C for 1.5 hr. The mixture was diluted with water and evaporated; the residue was recrystallized from CH_3OH/H_2O.

Amino ester oligomer came from distilled V ($R' = CH_3$) that solidified in two weeks at 20–25 C in a closed vial, and after 11 weeks the dried solid (mp 80–138 C) analyzed as the oligomer with an average of 2.5 monomer units (5). Exposure to CO_2 for 3 hr converted the 2.5-unit oligomer to the carbamate, as shown by analysis. The resin left in the still pot from the amino ester distillation was an oligomer with about 10 units, after reprecipitation from 90% HCOOH.

Polymerization of 9-Aminononanamide (IV)

In Water. A solution of 1.07 g amino amide (15.16% N, 0.00578 mole, DTA 83 C) in 20 ml H_2O was heated in a 240 ml glass-lined autoclave at 250 C for 2.2 hr. After venting the steam (30 min) at 250 C into a condenser under N_2 and holding 30 min at 250 C (1 atm N_2), the autoclave was closed and cooled to 10 C. The vent condensate contained 0.00528 equivalent titratable base (91.3% theory NH_3). The friable, pale yellow, polymeric product (0.96 g, mp 170–176.5 C) was purified by reprecipitation (10 ml CF_3CH_2OH, 220 ml H_2O). The recovered polymer (mp 160–177 C, DTA 165 and 177 C, intrinsic viscosity 0.265 in CF_3CH_2OH) analyzed as a nylon-9 having 12 monomer units. Further polymerization at 0.02 mm for 4.0 hr at 30–220 C and 5.1 hr at 220-248 C

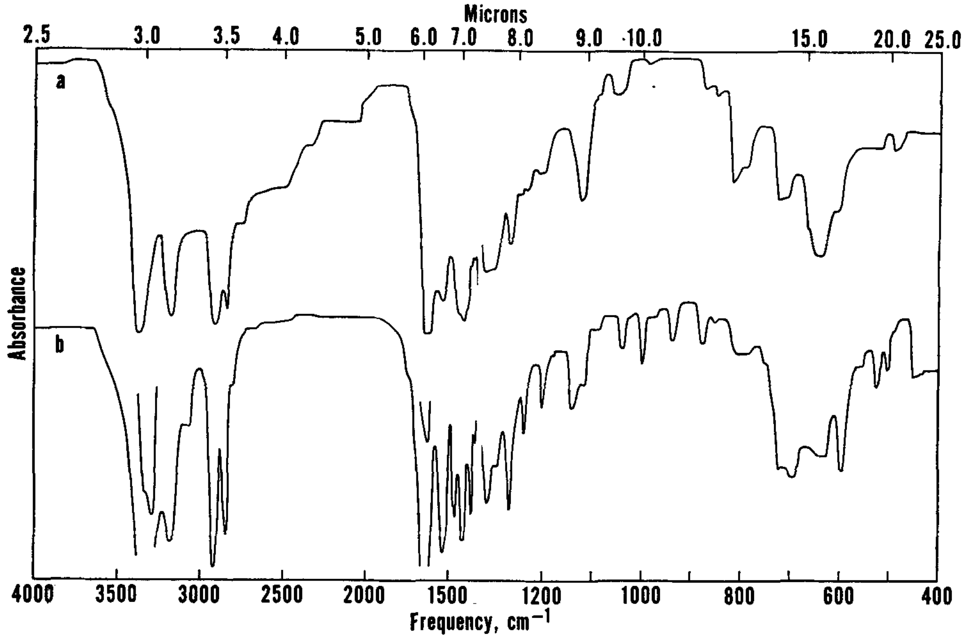

FIG. 5. Infrared spectra of (a) the carbamate salt of 9-aminononanamide and (b) 9-acetamidononanamide; 1% in KBr.

gave a hard amber resin containing 11% CF_3CH_2OH-insolubles. The IR spectrum of the soluble fraction (mp 167–179 C, intrinsic viscosity 0.433 in CF_3CH_2OH) closely matched that of high mol wt nylon-9 (VII) made from the amino acid.

Anhydrous polymerization of amino amide carbamate at 250–260 C under N_2 for 13 hr gave only a trimer (mp 105–138 C, 11.1% N). Heating XIV at 235–250 C for 8 hr (NH_3 evolved) gave a gray tetramer (carbamate mp 160–172 C, DTA 174 C, after reprecipitation from HCOOH). Compound XV gave a similar product (mp 152–165 C) at 224–230 C for 5 hr.

9-Aminononanoic Acid from Hydrolysis of Amino Amide

A solution of 0.67 g crude XVI (10.4% N, 0.00249 mole) in 50 ml 12 N HCl was refluxed overnight and then evaporated. Crude amino acid (0.435 g, 100% yield, 98% pure by CHN analysis) was recovered from the residue with a polyamine-type ion-exchange resin. Recrystallization of 0.38 g from 25 ml H_2O and 25 ml acetone (cooled to 0 C) yielded 0.28 g pure 9-aminononanoic acid (mp 176–181 C, DTA 193 C). Hydrolysis of the amino amide in water alone was slow; after 41 hr at 90 C the reaction was 32% complete.

Results and Discussion

Three routes from soybean oil to the amino amide (Fig. 1, IV) were demonstrated; alkyl soyate, aldehyde oil or soybean amides served as the intermediates. These provide additional syntheses of nylon-9 from soybean oil, and a new intermediate for 9-aminononanoic acid, the preferred monomer. The fundamental reactions in each route were: (a) reductive ozonolysis of the C_9 double bond to aldehydes (12,13); (b) reductive amination of aldehyde to aminomethyl (14,17); and (c) ammonolysis of ester to amide. These reactions are capable of 90–100% yields.

The amino amide was converted directly to low molecular weight nylon-9 and, also, was hydrolyzed readily to 9-aminononanoic acid, which gives much higher molecular weight polymer (3). The yields in many of these exploratory reactions did not attain the 90–100% level reported for simpler analogous systems. However, the key reductive amination step did proceed in 98% yield with MAZ in CH_3OH at 60 C/1000 psi and in >90% yield with azelaaldehydamide in CH_3OH at 50–90 C/1500–2000 psi. Ammonolysis was low in the MAZ experiment because of low temperature, reaction time (3 hr), or both, but went in >90% yield with aldehyde oil at 125–130 C in 1-propanol or in anhydrous ammonia alone. Isolation of intermediate aldehyde in the olefin → amine sequence can be omitted (18,20).

9-Aminononanamide (IV) via Alkyl Azelaaldehydates

Preparation of IV from soybean oil via III utilizes intermediates that are readily purified by distillation (3), but it has the most steps if amination and ammonolysis are carried out in two separate reactions. Reductive amination of III ($R' = CH_3$) went in 98% yield, but the isolated yield of the amino ester (V, $R' = CH_3$) was cut to 19% by simultaneous ammonolysis, and also by polymerization during distillation.

Simultaneous reductive amination and ammonolysis of III to IV went best in methanol, of the solvents tested; ammonium acetate was added as an ammonolysis catalyst. Some evidence was obtained that 9-aminononanoic acid is a slightly better catalyst

TABLE I
Properties of 9-Aminononanamide and Derivatives

Compound	Formula	Melting point, C		Description	Elemental analysis, %					
					Theory			Found		
		Hot stage	DTA peak		C	H	N	C	H	N
I	$O = CH(CH_2)_7CONH_2$	50– 75	......	Microflakes	62.39	11.05	8.08	62.59	11.03	8.17
X	$HON = CH(CH_2)_7CONH_2$	118–125	130	Powder	66.01	11.39	12.83	65.82	11.28	12.45
XI	$H_2NCONH{-}N = CH(CH_2)_7CONH_2$	162–167	179	Microflakes	66.63	11.18	8.18	67.26	11.07	8.06
IV	$H_2N(CH_2)_8CONH_2$	60–130	74	Microflakes	64.25	10.51	7.68	62.57	10.56	7.97
				Powder	63.57	10.67	12.02	63.14	11.17	12.01
XII	$0.5\ CO_2 \cdot H_2N(CH_2)_8CONH_2$	102–117	148	Powder	59.03	10.13	9.38	58.83	10.45	10.45
XIII	$HCl \cdot H_2N(CH_2)_8CONH_2 \cdot 0.5H_2O$	150–157	159	Granules	64.83	10.61	11.61	64.36	10.46	10.71
XIV	$0.5\ ({-}COOH)_2 \cdot H_2N(CH_2)_8CONH_2$	190–196	204	Microcrystalline	51.97	8.36	5.05	51.94	8.18	4.98
XV	$({-}COOH)_2 \cdot H_2N(CH_2)_8CONH_2$	121–154	120	Unstable paste	63.13	10.01	8.18	63.73	10.24	7.18
XVI	$CH_3COOH \cdot H_2N(CH_2)_8CONH_2$	100–115	121	Microcrystalline	58.04	9.74	15.04	58.33	9.76	14.88
XVII	$CH_3CONH(CH_2)_8CONH_2$	132–137	137	Short needles	52.61	8.83	24.54	53.17	8.83	24.17
XVIII	$HO(CH_2)_8CONH_2$	106–112	112	Waxy, soluble polar						
XIX	$[H_2NCO(CH_2)_8]_2NH$	140–152	156	solvents	62.75	11.70	16.26	62.37	11.44	16.14
XX	$CH_3OOC(CH_2)_8NH(CH_2)_8CONH_2$	90– 93	87	Powder	58.73	10.38	14.42	59.44	10.14	14.74
XXI	$0.5\ CO_2 \cdot H_2N(CH_2)_8CONH(CH_2)_8COOCH_3$	95–155	98,117,(149)	Microcrystalline	49.65	10.18	12.86	50.12	10.62	12.24
XXII	$0.5\ CO_2 \cdot H[{-}NH(CH_2)_8CO{-}]_2NH_2$	134–140	156	Flakes	55.28	9.74	12.89	55.28	9.52	12.75
XXIII	$(CH_3COOH)_2 \cdot H[{-}NH(CH_2)_8CO{-}]_2NH_2$	126–138	136	Microcrystalline	50.37	8.45	10.68	50.29	8.57	10.81
XXIV	$CH_3CO[{-}NH(CH_2)_8CO{-}]_2NH_2$	142–162	159	Needles	56.87	10.41	12.06	57.07	10.39	12.15
XXV	$({-}COOH)_2 \cdot H_2N(CH_2)_8COOCH_3$	102–128	105,117,157	Granules	61.65	10.35	13.07	61.60	10.45	13.20

(63% vs. 50% in limited testing), although it does not form an isolable ammonium salt. Ammonolysis was very slow in dioxane, anhydrous ammonia alone, or without a catalyst. Simultaneous reductive amination and ammonolysis have been reported in the formation of 10-aminodecanamide in 70% conversion from ethyl sebacaaldehydate in ethanol at 150 C, but not in the analogous reaction with MAZ (18).

9-Aminononanamide (IV) via Aldehyde Oil

The shortest route to IV is that via II in aldehyde oil and provides a four-step synthesis of nylon-9 from soybean oil. The best second step occurred in one experiment in ethanol/*n*-heptane, which gave a 56% conversion of II to IV as a two-stage reaction: the reductive amination stage at 40–70 C/1500 psi for 1.5 hr to minimize aldehyde side reactions, and the subsequent ammonolysis stage at 125 C/2000 psi for 3.3 hr.

A variety of solvents was suitable for the II → IV reaction, including anhydrous ammonia alone, alcohols, and benzene-water. Although aldehyde oil formed an insoluble gel instantly when exposed to ammonia vapor, stirring into excess ammonia in alcohol gave no gel. In addition to Raney nickel, 5% $Pd/BaSO_4$ was also scouted as the reduction catalyst, giving about 7% conversion to IV in benzene-water at 70 C/1500 psi/1 hr and 140 C/2000 psi/1 hr, and over 27% in ammonia alone at 55–70 C/1500 psi/1.5 hr and 130 C/2300 psi/2.3 hr. Such noble metal catalysts should prevent the metal complex formation observed with nickel.

9-Aminononanamide (IV) via Soybean Amides

Azelaaldehydamide (I) was obtained from soybean amides in 25–62% conversion by reductive ozonolysis. Evidence for slight instability of I was obtained when stripping at 40 C gave a 37% lower –CHO titer in crude I than at 25 C. The –CHO loss may be due to reaction with $-CONH_2$ groups to form alkylidene-bis-amides (20):

$$RCHO + 2R'CONH_2 \longrightarrow (R'CONH\text{–})_2CHR + H_2O$$

High overall yields of IV from soybean amides should be feasible by prompt use of I without isolation. Although pure I was not isolated, samples of its pure oxime and semicarbazone were prepared (Table I).

Properties of 9-Aminononanamide (IV)

The amino amide is a strongly basic waxy solid that is very soluble in water (Fig. 4). The true melting point (74 C by DTA) is slightly higher than that of the 8- or 10-carbon homolog (11,19). Hot-stage melting points were irregularly higher, apparently due to absorption of 0.5 mole atmospheric carbon dioxide to form a carbamate, $H_2NCO(CH_2)_8NHCOOH \cdot H_2N(CH_2)_8CONH_2$, mp 102–117 C, DTA 149 C. Other derivatives are listed in Table I; representative thermograms are shown in Figure 2, and infrared spectra in Figure 5.

The infrared spectrum (Fig. 3) of the amino amide was in harmony with its assumed structure. The high frequency ($890\ cm^{-1}$) of the amine N–H out-of-plane deformation band indicates strong H-bonding (21); the band was absent in the melt at 92 C and in the carbamate.

The amino amide, isolated as its acetate salt from runs utilizing ammonium acetate as catalyst, was readily separated from its salts or nonbasic impurities by ion-exchange.

Hydrolytic polymerization (5,10,11) of IV yielded nylon-9 having $\eta = 0.43$. Anhydrous polymerization of the amino amide or its oxalate (22) gave only low oligomers (D.P. 3–4), perhaps because unreactive nitrile end-groups are formed.

The amino amide was readily hydrolyzed to 9-aminononanoic acid (VI) with hydrochloric acid at 90 C (23), but slowly in water alone. Since the amino acid is easily recrystallized, a feasible route to nylon-9 from soybean oil may be via IV and VI.

Related Compounds

Side-reactions during the formation of the amino amide, such as $-CHO \rightarrow -CH_2OH$ or $(-CH_2-)_2NH$, were effectively inhibited by a large excess of ammonia (40–150 NH_3/–CHO). The minimum ratio was not determined; lower ratios have been reported (18,19). The two expected by-products, 9-hydroxynonanamide and bis(8-carbamoyloctyl)amine, were prepared and characterized. The secondary amine was not detected among amino amide by-products, and the hydroxy amide was formed only in trace amounts (<3%).

Small amounts of dimeric products were formed in amino amide syntheses from II or III when ammonolysis was incomplete, presumably during workup. Aminolysis of unchanged ester groups can occur with the amino ester or amino amide:

$$\begin{gathered} 2H_2N(CH_2)_8COOCH_3 \longrightarrow \\ H_2N(CH_2)_8CONH(CH_2)_8COOCH_3 + CH_3OH \\ \text{(VIII)} \\ H_2N(CH_2)_8COOCH_3 + H_2N(CH_2)_8CONH_2 \longrightarrow \\ H_2N(CH_2)_8CONH(CH_2)_8CONH_2 + CH_3OH \\ \text{(IX)} \end{gathered}$$

Both reactions were observed during workup of the products from the reaction sequence, III ($R' = CH_3$) → IV.

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REFERENCES

1. Deanin, R. D., Soc. Plast. Eng. J., *1967,* 44–47.
2. Horn, C. F., B. T. Freure, H. Vineyard and H. J. Decker, J. Appl. Polym. Sci. *7,* 887–896 (1963).
3. Miller, W. R., E. H. Pryde, D. J. Moore and R. A. Awl, Amer. Chem. Soc. 1967 Fall Meeting, Div. Org. Coatings Plastics Chem. Preprints *27*(2), 160–167 (1967).
4. Carothers, W. H. (E. I. du Pont de Nemours and Co., Inc.), U.S. Patent 2,071,253 (1937).
5. Coffman, D. D., N. L. Cox, E. L. Martin, W. E. Mochel and F. J. Van Natta, *J. Polym. Sci. 3, 85–95 (1948).*
6. Otsuki, H., and H. Funahashi, U.S. Patent 2,862,940 (1958).
7. Otsuki, H., and H. Funahashi, Advan. Chem. Ser. *21,* 205–208 (1959).
8. Komoto, H., and K. Saotome, Kogyo Kagaku Zasshi *66,* 1728–1732 (1963); Resins, Rubbers, Plastics *4,* 2317–2319 (1964).
9. Pryde, E. H., and J. C. Cowan, Amer. Chem. Soc. 154th Meeting, Div. Chem. Mktg and Econ. Preprints *8*(2), 130–143 (1967).
10. Algem. Kunst. Unie N.V., British Patent 627,596 (1949).
11. Chiusoli, G. P., and P. Perrazzoni (Montecatini), U.S. Patent 3,235,576 (1966).
12. Moore, D. J., E. H. Pryde and J. C. Cowan, JAOCS *42,* 894–898 (1965).
13. Pryde, E. H., D. E. Anders, H. M. Teeter and J. C. Cowan, Ibid. *38,* 375–379 (1961).
14. Anders, D. E., E. H. Pryde and J. C. Cowan, Ibid. *42,* 824–827 (1965).
15. Pryde, E. H., C. M. Thierfelder and J. C. Cowan, *JAOCS 44,* 366A, Abstr. 62 (1967).
16. Pryde, E. H., D. E. Anders and J. C. Cowan, Ibid. *42,* 454A, Abstr. 47 (1965).
17. Omote, Y., K. Iwase and J. Nakamura, Kogyo Kagaku Zasshi *70,* 1335–1338 (1967); Chem. Abstr. *68,* 29066 (1968).
18. Pollart, K. A., and R. E. Miller, J. Org. Chem. *27,* 2392–2394 (1962).
19. White, R. W., and J. L. O'Brien (Rohm and Haas Co.), U.S. Patent 3,350,455 (1967).
20. Noyes, W. A., and D. B. Forman, J. Amer. Chem. Soc. *55,* 3493–3494 (1933).
21. Bellamy, L. J., "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, 1958, p. 256.
22. Moldenhauer, O., R. Zoller and G. Trautmann (Phrix-Werke A.-G.), German Patent 914,187 (1954).
23. Bolton, P. D., and G. L. Jackson, Aust. J. Chem. *22,* 527–532 (1969).

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