# Reactions of Azelaaldehydic Esters[1]

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## Abstract

Alkyl azelaaldehydates and their acetals can undergo reactions at either the aldehyde or the ester group to form a variety of novel and reactive monomers and polymers. Pertinent reactions of the aldehyde group (and resultant products) include acetalization with pentaerythritol (diester-acetal), acetalization with glycerol (hydroxy ester-acetal), hydrogenation (hydroxy ester), reductive alkylation of ammonia (amino acid and imino diester), aldolization (dibasic acid) and hydrazone formation (azine dibasic acids). Reactions at the ester group include aminolysis (diacid amides) and hydrazinolysis (hydrazide acetal). These various products can undergo self-condensation or condensation with glycols or diamines to form polyesters, polyamides, poly(ester-acetals) and poly(amide-acetals). Polymers with cyclic acetal structures in the polymer backbone have latent crosslinking capabilities.

## Introduction

Alkyl azelaaldehydates are intriguing bifunctional compounds that can be prepared readily by reductive ozonolysis of unsaturated fatty esters. They have been known for some 60 years (6,15). Little has been done to exploit their extraordinary versatility, except for the work at the Northern Regional Research Laboratory. Announcement that methyl azelaaldehydate (MAZ) and its dimethyl acetal (MAzDA) are potentially low-cost intermediates will encourage others to explore their reactions (1). Among the more important reactions are those leading to many different monomers and polymers. Summarized here are the results of investigations on the chemistry of azelaaldehydates as developed by the Northern Laboratory. To make this summary as complete as possible, our published and recently reported data are presented as well as unpublished data.

## Discussion

Reactions of azelaaldehydic esters include acetalization, transacetalization, reduction, reductive alkylation, aldolization, hydrazinolysis and aminolysis with diamines. These will be described under the individual reaction products.

### Pentaerythritol Acetal

This cyclic diacetal of MAZ may be prepared either by direct acetalization or, preferably, by transacetalization with MAzDA (17). The product is a diester having a spiro acetal structure and is a dl-mixture (Fig. 1). The diester can easily be saponified to a diacid. In the presence of an alkaline catalyst, the diester condenses with glycols to form poly(ester-acetals) (17). Poly(amide-acetals) are formed from the diacid and diamines (18). These linear polymers can be crosslinked by several methods to insoluble and infusible materials. Crosslinking at high temperatures (ca. 275 C) in the presence of metal oxides or salts (e.g., litharge, zinc acetate) or an acid, such as *p*-toluenesulfonic, results in a product strongly adherent to glass and metal (14). The crosslinking reaction is believed to involve acetal oxygen bonds. The high temperature required for crosslinking and the resultant discoloration are disadvantages that may hinder utility of these products. Crosslinking with peroxide probably involves the acetal proton (11). The properties of poly(ester-acetals) crosslinked with peroxide are considerably different compared to those crosslinked catalytically with metal oxides or salts (Table I). A third possible crosslinking method, but one we have not tested, is radiation (5).

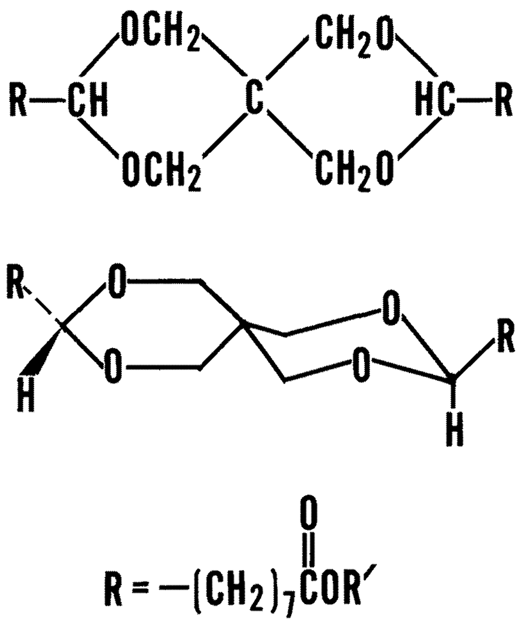

FIG. 1. Structure of pentaerythritol acetal of methyl azelaaldehydate.

### Isopropylideneglycerol Ester

This ester of azelaaldehydic acid dimethyl acetal readily forms by interesterification of MAzDA with isopropylideneglycerol. Hydrolysis of the ketal and acetal groups does not yield the expected monoglyceride of azelaaldehydic acid but a low-molecular weight polymer resulting from self-acetalization (12). This hydrolysis-polymerization is carried out in benzene solution with concentrated hydrochloric acid at 7–9 C (Fig. 2). Under such conditions there is obtained a viscous polymeric oil having 6–7 repeating units. The competitive, but slower, hydrolytic cleavage of the ester functionality is the terminating reaction. The sodium salt of this polymer is a white, water-soluble solid melting at 110 C and having some surface-active properties.

TABLE I
Crosslinked Poly(ester-acetals)

| Property | | Method and conditions | |
|---|---|---|---|
| | | Peroxidic<br>150 C, 30 min | Catalytic<br>275 C, 30 min |
| Adherence to glass | | Poor | Excellent |
| Hardness | | Soft | Hard |
| Color | | Good | Brown |
| Alkali | Resistance | Excellent | Fair |
| Acid | Resistance | ........ | Excellent |
| Chloroform | Resistance | Poor | Excellent |

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[1] Presented at the AACC-AOCS Joint Meeting, Washington, D.C., April, 1968.

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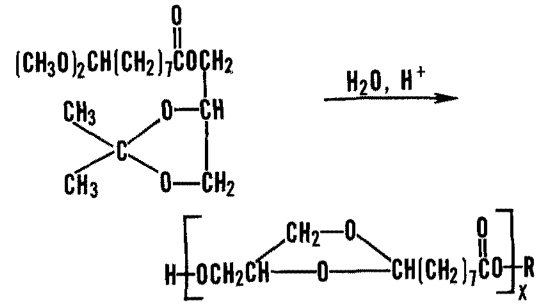


FIG. 2. Hydrolysis-polymerization of isopropylideneglycerol azelaaldehydate dimethyl acetal. Number of repeating units, n, is 6–7.

**Glycerol Acetals**

Selective glycerolysis at the acetal functionality of MAzDA is readily carried out (20). This selectivity again illustrates the greater rates of acetal reactions as compared to ester reactions (17,19). GLC analysis of the product revealed four isomers (Fig. 3) (8), presumably *cis* and *trans* isomers of the 5- (dioxolan) and 6- (dioxan) membered cyclic acetal compounds. Isolation of the pure isomers was accomplished by preparative GLC or dry-column chromatography (9).

IR and NMR spectral data aided structural assignments for the four isomers. IR absorption occurred in two regions for the hydroxyl stretching frequency: at the 3630–3640 $cm^{-1}$ region characteristic of free hydroxyl and at the 3585–3600 $cm^{-1}$ region characteristic of associated hydroxyl groups (Table II). Isomer A showed no free hydroxyl absorption, probably because of strong intramolecular bonding. Absorption characteristic of associated hydroxyl was not detected for isomer D. Absorption in the free hydroxyl range for this isomer was 10 wave numbers below that for isomers B and C, indicative of a secondary hydroxyl group for isomer D.

NMR spectral data for model compounds showed that the chemical shift for the dioxolan acetal proton occurred at a field position lower than that for the dioxan acetal proton, and therefore this assignment was made for the glycerol acetals (Table III). Doublets for the hydroxyl proton result from the secondary alcohol structure in the dioxan ring.

On the basis of this spectral behavior and other physical data, we have made structural assignments as illustrated in Figure 4 (8). Isomer A, the first to be eluted from the GLC column, is the *cis*-dioxan with the respective hydroxyl and alkyl groups either axial and equatorial or equatorial and axial. Although the first structure with the axial hydroxyl group would be favored for strong intramolecular hydrogen bonding, NMR does not confirm the axial acetal proton. The two forms may be rapidly interconverting (4). Isomers B and C are the *cis*- and *trans*-dioxolans.

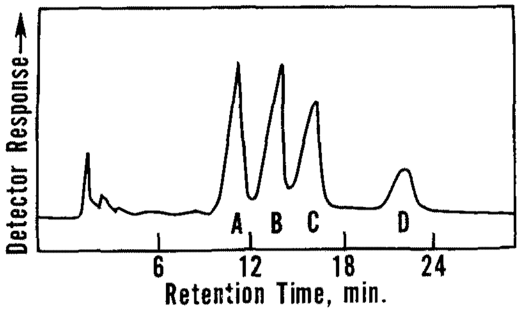


FIG. 3. Chromatogram of the glycerol acetals of methyl azelaaldehydate.

TABLE II

Glycerol Acetals IR Absorption Data

| Isomer[a] | OH Bands, $cm^{-1}$ | |
|---|---|---|
| | Free | Associated |
| A | Absent | 3585 m[b] |
| B | 3640 vw | 3597 w |
| C | 3640 vw | 3600 w |
| D | 3630 w | Absent |

[a] 50–60 mg/ml in carbon tetrachloride.
[b] vw, very weak; w, weak; m, medium absorption.

Exact identification of the isomers was not possible because of difficulties in isolating a sufficient sample. The D isomer, the last to be eluted from the GLC column, is the *trans*-dioxan and has both hydroxyl and R groups in the equatorial position. The structure with both groups in axial positions is conformationally unstable. These assignments are consistent with previous ones given analogous cyclic glycerol acetals (2).

Polymers from the different geometric isomers had widely different melting temperatures (Table IV) (8). The polymers from the unsymmetrical, dioxolan monomers had a low degree of crystallinity and were low melting. The symmetrical, 6-membered ring in isomers A and D gave polymers of high crystallinity. The melting point of 150 C is high for an aliphatic polyester and can be attributed to the rigid ring structure. NMR spectral data indicated that these polymers have retained their structural identity. Polymerization of the isomeric mixture of glycerol acetals yielded polymers melting as high as 115–120 C but usually in the range of 44 to 57 C depending on polymerization conditions. Polymerization catalyzed by lead acetate at 150–190 C gave a noncrystalline polymer containing about three parts of dioxolan units to one part of dioxan acetal units. Surprisingly, this polymer crystallized slowly upon standing; the crystallized polymer had a melting range corresponding to that of the polymer prepared at 260–290 C with lime catalyst and to that of the polymer from the B and C isomers. These last two polymers had a much higher dioxolan/dioxan ratio, ranging from 5–10 parts of the 5-membered ring for each 6-membered ring. Evidently, the crystalline regions consist of the dioxolan units, and isomer B is isomorphous with isomer C, but these are not isomorphous with the 6-membered ring.

These poly(ester-acetals) possess latent crosslinking functionality as do those from pentaerythritol acetals.

**9-Hydroxynonanoates**

Alkyl soyate hydroperoxidic ozonolysis products may be reduced to give the hydroxy ester instead of the aldehyde ester (Fig. 5) (10,21). This simple hydroxy ester may be as easily condensed to a polyester as the glycerol acetal of MAZ. Indeed, the presence of an inorganic salt during attempted distillation results in almost complete polycondensation and little distilled product. In the absence of catalyst, distillation proceeds normally under vacuum. We have not yet characterized these polyesters, which do

TABLE III

Glycerol Acetals NMR Spectral Data

| Isomer | Resonant frequency, mcps | Solvent | Chemical shift, τ | |
|---|---|---|---|---|
| | | | Acetal | Hydroxyl |
| B,C | 100 | $CDCl_3$ | 5.10 (t) | 7.17 |
| | | DMSO | ...... ...... | 6.22 |
| A | 60 | $CDCl_3$ | 5.43 (t) | 6.58 |
| | | DMSO | ............ | 5.20 (d) |
| D | 60 | $CDCl_3$ | 5.60 (t) | 6.51 |
| | | DMSO | ............ | 4.95 (d) |

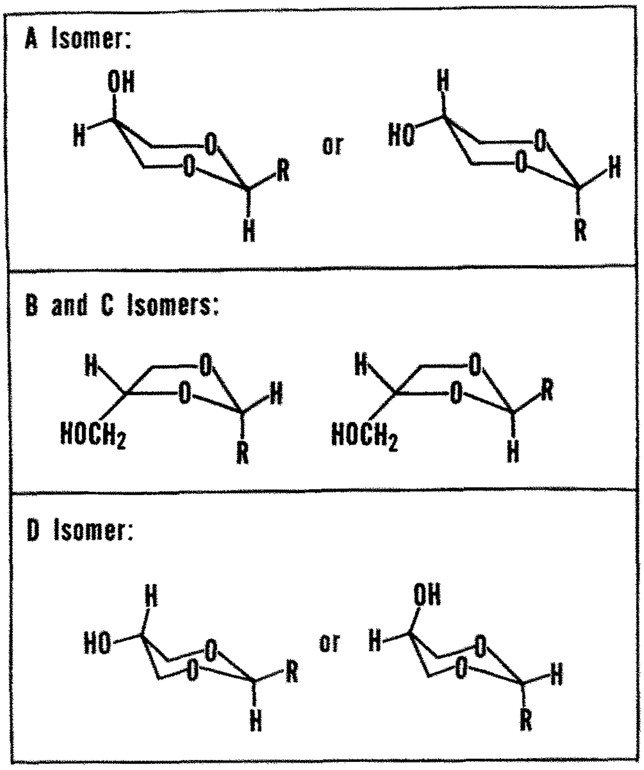


FIG. 4. Structural assignments for the glycerol acetals of methyl azelaaldehydate: A, *cis*-dioxan isomer; B and C, *cis*- and *trans*-dioxolan isomers; D, *trans*-dioxan isomer.

not possess the latent crosslinking properties characteristic of poly(ester-acetals).

**Alkyl 9-Aminononanoates**

We have recently described the preparation of 9-aminononanoic acid and of the polyamide nylon-9 therefrom (13). The amino acid preparation involves reductive alkylation of ammonia with MAZ over a nickel catalyst according to the equation (3):

$$ROCO(CH_2)_7CHO + NH_3 + H_2 \xrightarrow{Ni} ROCO(CH_2)_7CH_2NH_2 + H_2O$$

The amino ester is too self-reactive to be isolated readily but can be converted immediately to the stable amino acid by hydrolysis.

The amino acid undergoes self-condensation under typical polymerization conditions to give a fiber-forming polyamide:

$$n\ H_2N(CH_2)_8COOH \xrightarrow{\Delta} H\left[HN(CH_2)_8CO\right]_n OH + (n\text{-}1)H_2O$$

This polyamide, nylon-9, has the highest melting point (205 C) of the low moisture-absorbing aliphatic nylons (nylon-8 and the higher numbered nylons). Low moisture absorption allows better dimensional stability, improved electrical properties and superior wash-wear properties.

TABLE IV

Glycerol Acetal Polymers[a]

| Monomer | | Polymer | |
|---|---|---|---|
| Ring size | Isomer | MW | mp, C |
| 5 | *cis* and *trans* | 4100 | 54 |
| 6 | *cis* | 5500 | 120 |
| 6 | *trans* | 6800 | 150 |
| 5,6 | *cis* and *trans* | 7500 | 49 |

[a] Polymerized in bulk with calcium oxide catalyst by heating at 250–280 C under vacuum.

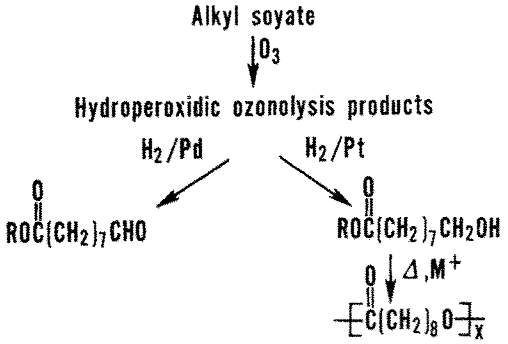


FIG. 5. Catalytic hydrogenation of alkyl soyate ozonolysis products to aldehydes and to alcohols.

**Iminodiesters**

In the reductive alkylation of ammonia as described above, an excess of ammonia leads to the primary amine in good yield. With nearly stoichiometric quantities of ammonia, the secondary amine (an iminodiester) is formed also in good yield according to the equation (16):

$$2\ ROCO(CH_2)_7CHO + NH_3 + 2H_2 \xrightarrow{Ni} ROCO(CH_2)_8NH(CH_2)_8COOR + 2H_2O$$

We plan to investigate some of the reactions possible for this iminodiester.

**Aldol Product**

Under mildly alkaline conditions, MAZ condenses with itself to form an aldol condensation product. Elemental analysis indicates that some crotonization also occurs.

**Azine**

Hydrazine reacts with MAZ to form the azine, a diester, in accordance with the following equation:

$$OCH(CH_2)_7COOCH_3 + H_2NNH_2 \longrightarrow CH_3OCO(CH_2)_7CH{=}N\text{–}N{=}CH(CH_2)_7COOCH_3 + 2H_2O$$

This diester is thermally stable to at least 200 C since it was successfully distilled under vacuum. We have not yet investigated reactions of this diester.

**Hydrazide**

Hydrazinolysis of the ester group in MAzDA leaves the acetal group unchanged:

$$(CH_3O)_2CH(CH_2)_7COOCH_3 + H_2NNH_2 \longrightarrow (CH_3O)_2CH(CH_2)_7CONHNH_2 + CH_3OH$$

The hydrazide is only slightly soluble in cold water but very soluble in hot water. Aqueous solutions of the hydrazide precipitate a polymer when hydrochloric acid is added:

$$(CH_3O)_2CH(CH_2)_7CONHNH_2 + H_2O \xrightarrow{H^+} OCH(CH_2)_7CONHNH_2 + 2CH_3OH$$

$$n\ OCH(CH_2)_7CONHNH_2 \longrightarrow O{=}\left[CH(CH_2)_7CONHN\right]_n H_2 + (n\text{-}1)H_2O$$

**Bis(amide-esters)**

Bis(amide-esters) of the type $ROOC(CH_2)_7CONHXNHCO(CH_2)_7COOR$ were synthesized to determine if regularly alternating copolymers could be prepared from them. Two routes to the bis(amide-esters) are possible. One route entails aminolysis of MAzDA with a diamine, hydrolysis of the acetal groups, oxidation of the resulting dialdehyde to a diacid and finally esterification if desired.

Alternatively, the aminolysis could be carried out on an unsaturated fatty ester and the resulting diamide oxidatively cleaved to a diacid-diamide with

TABLE V

Diamides and Diacid-Diamides From Methyl Oleate (MO) ($RCOOCH_3$)

| Diamine (X) | Diamide Key | Diamide ($RCONH\text{-}X\text{-}NHCOR$) mp, C | Diacid-diamide [$HOOC(CH_2)_7CONH\text{-}X\text{-}NHCO(CH_2)_7COOH$] Key | Yield | mp, C | Dimethyl ester-diamide mp, C |
|---|---|---|---|---|---|---|
| Ethylene diamine | Ia(MO) | 114–115 | IIa(MO) | 66 | 130–132 | 124–125 |
| Hexamethylene diamine | Ib(MO) | 108–109 | IIb(MO) | 67 | 152–153 | 114–116 |
| 1,4-Bis(aminomethyl)-cyclohexane | Ic(MO) | 135–138 | IIc(MO) | 59 | 168–170 | 144–147 |

ozone. The reactions may be illustrated with methyl oleate [$R = CH_3(CH_2)_7CH = CH(CH_2)_7–$]:

$$2\ RCOOCH_3 + H_2N\text{–}X\text{–}NH_2 \longrightarrow RCOHN\text{–}X\text{–}NHCOR + 2CH_3OH$$

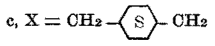
I

$$RCONH\text{–}X\text{–}NHCOR \xrightarrow{O_3} 2CH_3(CH_2)_7COOH + HOOC(CH_2)_7CONH\text{–}X\text{–}NHCO(CH_2)_7COOH$$

II

a, $X = (CH_2)_2$

b, $X = (CH_2)_6$



This latter route was selected for our investigations as being more direct. As starting materials, methyl oleate, methyl soyate and soybean oil were used. Soybean oil gave somewhat lower yields of diamides than methyl soyate or methyl oleate. Since methyl soyate (and soybean oil) has about 15% of saturated fatty acids (methyl palmitate and stearate), some diamides were formed with one unsaturated and one saturated fatty acid. Ethylene and hexamethylene diamines and 1,4-bis(aminomethyl)cyclohexane were used to make the diamides (Table V). Ozonolyses were carried out in chloroform, a good solvent for the otherwise difficultly soluble diamides. Oxidation of the ozonolysis products was accomplished with hydrogen peroxide and formic acid (Table V). Preliminary data indicate that the properties of the regularly alternating copolyamides and copoly(esteramides) prepared from these materials are considerably different from those of corresponding random polymers (Table VI).

## Experimental Procedures

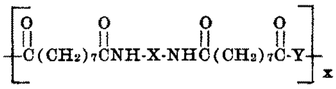
### Aldol Condensation

This reaction was carried out according to a procedure previously reported for ethyl adipaldehydate (7). MAZ (9.3 g, 0.05 g mole) in 30 ml of diethyl ether was added dropwise over a period of 2 hr to 30 ml of 2 N NaOH at −5 to −8 C with stirring. Methylene chloride extraction of the solution after acidification with 1 N hydrochloric acid to the methyl orange end point gave 4.78 g (51% yield) of an oil. Methylene chloride extraction before acidification gave about 1 g of an oil, an amount which indicated that saponification of the methyl ester had occurred to a large extent.

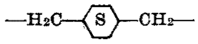
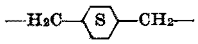
*Analysis.* Calculated for $C_{18}H_{32}O_6$: C, 62.76; H, 9.36; carbonyl equiv., 8.13; neutral equiv., 172.2. Calcd for $C_{18}H_{30}O_5$: C, 66.23; H, 9.26; carbonyl equiv., 8.58; neutral equiv., 163.2. Found: C, 63.76; H, 9.15; carbonyl equiv., 7.66; neutral equiv., 172.6.

TABLE VI

Regularly Alternating Copolymers



$$\left[ \overset{O}{\overset{\|}{C}}(CH_2)_7\overset{O}{\overset{\|}{C}}NH\text{-}X\text{-}NH\overset{O}{\overset{\|}{C}}(CH_2)_7\overset{O}{\overset{\|}{C}}\text{-}Y \right]_x$$

| Reactant[a] | X | Y | Copolymer mp, C |
|---|---|---|---|
| IIa(MO)[b] | $—(CH_2)_2—$ | $—OCH_2CH_2O—$ | 143–150 |
| IIa(MS) | $—(CH_2)_2—$ | $—NHCH_2CH_2NH—$ | 220–230 |
| IIb(MO) | $—(CH_2)_6—$ | $—NHCH_2CH_2NH—$ | 108–113 |
| IIc(EMO) |  | $—OCH_2CH_2O—$ | 235–245 |
| IIc(EMO) |  | $—NHCH_2CH_2NH—$ | 240–245 |

[a] As the dimethyl ester.
[b] MO, methyl oleate; MS, methyl soyate; EMO, Emersol methyl oleate.

### Azine

To 3.7 g of MAZ (0.02 g mole) in a round-bottomed flask was added with stirring a solution of hydrazine (0.38 g of 85% material, 0.01 g mole) in 15 ml of absolute ethanol. The solution was stored overnight in a refrigerator and then filtered to remove a small amount of some fine, dense crystals which melted over a wide range (75–105 C). The solution was evaporated under vacuum to give 3.38 g of a yellow product melting at about 21 C. Upon distillation under vacuum, the first fraction (0.73 g) boiled 73–81 C at 0.07 mm, $n_D^{30} = 1.4364$, and the second fraction (1.52 g, 41%) boiled 176–208 C at 0.05 mm, $n_D^{30} = 1.4689$, mp 24–32 C. After several recrystallizations from 50% ethanol and one from pentane-hexane, the analytically pure solid melted at 31–33 C.

*Analysis.* Calculated for $C_{20}H_{36}N_2O_4$: C, 65.18; H, 9.85; N, 7.60. Found: C, 64.99; H, 9.66; N (Dumas), 7.56.

### Hydrazinolysis

MAzDA (11.6 g, 0.05 g mole) and hydrazine (10 g, 0.25 g mole, of an 85% aqueous solution) were heated at 115 C for 15 min in a round-bottomed flask with agitation provided by a stream of nitrogen from a capillary tube. Sufficient alcohol was added to give a clear solution, and the solution was refluxed for 2 hr. The solvent and excess hydrazine were removed under vacuum in a water aspiratory rotary evaporator to a maximum temperature of 95 C to give 11.2 g of crude product (97% yield). Recrystallization from pentanehexane gave flat crystals that melted at 39.5–41 C.

*Analysis.* Calculated for $C_{11}H_{24}O_3N_2$: C, 56.87; H, 10.41; N, 12.06. Found: C, 57.11; H, 10.46.

### Diamides From Ethylene Diamine (Ia)

*From Soybean Oil.* Soybean oil (SO) (147.5 g) was heated at 135 C with ethylene diamine (15 g) and sodium methoxide (0.5 g of sodium in 15 ml of methanol) for 18 hr under nitrogen. The cooled product was dissolved in chloroform, washed with water and 10% hydrochloric acid and after drying the chloroform was removed. The product Ia(SO) was recrystallized from methanol and then acetone to give Ia (82.15 g; mp 111–119 C). Because of the low yield, methyl esters were used in later experiments.

*From Methyl Soyate.* Methyl soyate (MS) (147.5 g), ethylene diamine (15 g) and sodium methoxide

(0.5 g of sodium in 50 ml of methanol) were heated together under nitrogen at 135 C for 5 hr. The cooled product was dissolved in chloroform. This solution was washed with water and 10% hydrochloric acid and removal of chloroform left a solid, which was recrystallized from methanol and then acetone to give Ia(MS) (132.31 g; mp 110–119 C).

*From Pure (99%+) Methyl Oleate.* Methyl oleate (MO) (14.75 g), ethylene diamine (1.5 g) and sodium methoxide (0.05 g of sodium in 5 ml of methanol) were heated together under nitrogen at 130 C for 5 hr. The crude product was dissolved in chloroform, the solution was washed with water and 10% hydrochloric acid, and removal of the chloroform left crude Ia. Two recrystallizations from methanol gave Ia(MO) (10.82 g; mp 114–115 C).

*Analysis.* Calculated for $C_{38}H_{72}N_2O_2$: C, 77.45; H, 12.31; N, 4.76. Found: C, 76.76; H, 12.47; N, 4.61.

### Diamides From Hexamethylene Diamine (Ib)

*From Soybean Oil.* Soybean oil (74 g), 70% hexamethylene diamine (20.70 g) and sodium methoxide (0.5 g of sodium in 50 ml of methanol) were heated together under nitrogen at 135 C for 18 hr. The product was recovered in the usual manner and recrystallized from methanol to give Ib(SO) (42.3 g). The low yield confirmed the advisability of carrying out aminolysis on methyl esters rather than the glyceride.

*From Methyl Soyate.* Methyl soyate (74 g), redistilled hexamethylene diamine (bp 195–196 C) (15 g) and sodium methoxide (0.5 g of sodium in 50 ml of methanol) were heated together under nitrogen at 125 C for 24 hr. The cooled product was recrystallized from methanol to give Ib(MS) (68.21 g).

*From Pure Methyl Oleate.* Methyl oleate (99%+) (14.75 g), redistilled hexamethylene diamine (3.0 g) and sodium methoxide (0.05 g sodium in 5 ml of methanol), heated together under nitrogen at 130 C overnight. The product was recrystallized twice from methanol to give pure Ib(MO) (11.51 g; mp 108–109 C).

*Analysis.* Calculated for $C_{42}H_{80}N_2O_2$: C, 78.1; H, 12.50; N, 4.34. Found: C, 78.06; H, 12.31; N, 4.00.

### Diamides from 1,4-Bis(aminomethyl)Cyclohexane (Ic)

*From Emersol Methyl Oleate.* Emersol methyl oleate (EMO) (Emery Industries, 74 g), 1,4-bis(aminomethyl)cyclohexane (17.5 g) and sodium methoxide (0.5 g of sodium in 20 ml of methanol) were heated together under nitrogen at 130 C for 3 hr. Recrystallization of the product from methanol gave Ic(EMO) (68.1 g; mp 136–141 C).

*From Pure Methyl Oleate.* Methyl oleate (14.8 g), 1,4-bis(aminomethyl)cyclohexane (3.45 g) and sodium methoxide (0.1 g of sodium in 10 ml of methanol) were heated together under nitrogen at 135–140 C for 3 hr. The crude product was recrystallized twice from methanol to give pure Ic(MO) (12.12 g; mp 135–138 C).

*Analysis.* Calculated for $C_{44}H_{82}N_2O_2$: C, 78.67; H, 12.31; N, 4.17. Found: C, 78.35; H, 12.23; N, 3.94.

### Diacid-diamide from Ethylene Diamine (IIa)

Ia(MS) (33 g) was dissolved in chloroform (450 ml). The solution was cooled to 0 C, and ozone was bubbled through until an aliquot did not decolorize a solution of bromine in chloroform. This step was repeated with another 33 g of Ia(MS). The chloroform solutions were combined, and the chloroform was removed under reduced pressure at room temperature. The product was dissolved in formic acid (100 ml) and 30% hydrogen peroxide (150 ml) was added. The mixture was heated on a steam bath until a vigorous exothermic reaction started and then stored overnight at room temperature.

The mixture was filtered and the precipitate was triturated twice with ether (or until free from liquid monobasic acids), to give IIa(MS) (41.01 g; mp 127–132 C).

Similar treatment of 10 g of pure Ia(MO) gave 5.15 g of IIa(MO) melting at 130–132 C.

*Analysis.* Calculated for $C_{20}H_{36}N_2O_6$: C, 60.05; H, 9.07; N, 7.00. Found: C, 59.89; H, 9.11; N, 6.85.

### Diacid-diamide from Hexamethylene Diamine (IIb)

*From Methyl Soyate.* After ozonolysis as described above, Ib(MS) (32 g) gave IIb(MS) melting at 96–105 C (18.32 g).

*From Methyl Oleate.* Similar treatment of 11.51 g of Ib(MO) gave 5.52 g of IIb(MO) melting at 152–153 C.

*Analysis.* Calculated for $C_{24}H_{44}N_2O_6$: C, 63.10; H, 9.72; N, 6.13. Found: C, 62.41; H, 9.79; N, 5.31.

### Diacid-diamide From 1,4-Bis(aminomethyl)cyclohexane (IIc)

*From Emersol Methyl Oleate.* After ozonolysis and separation of pelargonic acid by trituration, Ic(EMO) (68.1 g) gave IIc(EMO) (35.41 g) melting at 137–150 C.

*From Pure Methyl Oleate.* Similar treatment on 12.12 g of Ic(MO) gave 3.56 g IIc(MO) melting at 168–170 C.

*Analysis.* Calculated for $C_{26}H_{46}N_2O_6$: C, 64.70; H, 9.54; N, 5.80. Found: C, 64.47; H, 9.45; N, 5.65.

### Esterification

IIc(EMO) (10 g) was dissolved in methanol (50 ml) and a drop of concentrated sulfuric acid was added. The mixture was refluxed for 2 hr. The cooled mixture was diluted with chloroform, washed with saturated sodium carbonate solution and dried. Removal of the solvents left a solid residue, which on recrystallization gave the diester (9.1 g; mp 144–147 C.

### Copoly(ester-amides)

Typically, the dimethyl ester of the diacid-diamide IIc(EMO) (2 g), ethylene glycol (0.48 g) and calcium oxide (0.03 g) were heated at 210 C for 2 hr under nitrogen and then at 250 C and 0.01 mm for an additional 3 hr. The resulting copoly(ester-amide) had a melting range of 235–245 C (Table VI).

### Copolyamides

Typically, the dimethyl ester of the diacid-diamide IIc(EMO) (2 g) and ethylene diamine (0.72 g) were heated under nitrogen for 3 hr with a gradual increase in temperature to 270 C. Heating was then continued at 240 C and 0.01 mm for an additional 2 hr. The resulting copolyamide melted at 240–245 C.

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