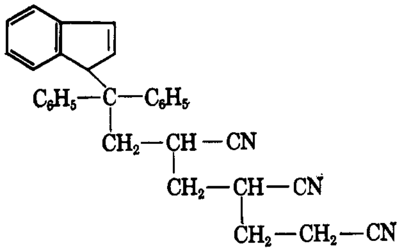

After recrystallization from 2-propanol the product weighed 140 g. (50%), m.p. 110–111° (lit.[23] m.p. 111°).

Electrolytic Reductive Coupling of 8,8-Diphenylbenzofulvene with Acrylonitrile.—The catholyte contained 11.5 g. (0.041 mole) of the fulvene, 23.1 g. (0.435 mole) of acrylonitrile, 82.3 g. of dimethylformamide, and 27.6 g. of 90.5% aqueous tetraethylammonium *p*-toluenesulfonate. The anolyte was 20 g. of 60% aqueous quaternary salt. Electrolysis was conducted at 40–45° at a controlled cathode voltage of −1.50 to −1.60 v. (s.c.e.). The amperage was gradually reduced from a high of 1.80 to 0.20 amp., total 2.27 amp.-hr. Acetic acid (1.80 ml.) was used for pH control. At the end of the run the mercury was separated and the brown-red catholyte was run dropwise with stirring into 300 ml. of water. The light yellow precipitate, after air drying overnight, weighed 29.0 g. It was extracted in a Soxhlet with methylene chloride for 11 hr. The insoluble portion was polyacrylonitrile[17]; the soluble material (10.8 g.), an amber sirup, was dissolved in methylene chloride and purified by passage through a column of activated alumina. The effluents were taken to dryness, the residue was digested with methanol, and the suspension was cooled at room temperature and filtered. For analysis a sample was dissolved in acetonitrile and filtered. Addition of methanol precipitated white crystals, m.p. 172–173°.

Anal. Calcd. for $C_{31}H_{27}N_3$: C, 84.32; H, 6.16; N, 9.52. Found: C, 84.07; H, 6.27; N, 9.57.

The proton magnetic resonance spectrum was determined under the conditions described above except that deuterated chloroform was used as the solvent. The proton of interest in this system is the olefinic proton in the five-membered ring of XIV. This proton appears in the spectrum as a singlet, δ −6.22. Dressler and Kurland[18] have observed this proton at δ −6.15 in an analogous system. The proton would have appeared as a multiplet had the isomer shown (left) been present.

Electrolytic Reductive Coupling of 9-Benzalfluorene and Ethyl Acrylate.—The catholyte contained 10.9 g. (0.0429 mole) of benzalfluorene, 42.6 g (0.426 mole) of ethyl acrylate, 27.8 g. of dimethylformamide, and 61.8 g. of 86.5% aqueous tetraethylammonium *p*-toluenesulfonate. The anolyte was 20 g. of a 60% aqueous solution of the quaternary salt. Electrolysis proceeded at 40° at a controlled cathode voltage of −1.50 to −1.55 v. (s.c.e.). The amperage was gradually reduced from 1.0 to 0.10 amp., total 2.1 amp.-hr. Acetic acid (1.70 ml.) was used to maintain the pH at *ca.* 8. The catholyte was then diluted with water, the mercury was separated, and 6.5 g. of 9-benzylfluorene, m.p. 133–134°, was removed by filtration. The mother liquor was extracted with four 50-ml. portions of methylene chloride. The extracts were washed and dried over Drierite. Volatile materials were removed on the water bath using an aspirator. The residue (5.4 g. of brown solid) yielded 2.2 g. of 9-benzylfluorene on fractional crystallization from methanol. The mother liquor was evaporated, and the residue was dissolved in methylene chloride and purified through alumina. The 2.04 g. of sirup obtained from the eluates was distilled; b.p. 204° (0.4 mm.).

Anal. Calcd. for XV, $C_{25}H_{24}O_2$: C, 84.23; H, 6.78. Found: C, 83.78; H, 6.79.

The infrared spectrum was consistent with the proposed structure.

Acknowledgment.—All instrumental analyses were performed by Donald Beasecker's group. The proton magnetic spectra were obtained and interpreted by Donald Bauer and Robert Anderson. Infrared spectra were interpreted by Ronald Coffey.

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[23] C. Weizmann, E. Bergmann, and M. Sulzbacker, *J. Org. Chem.*, **15**, 918 (1950).

Electrolytic Reductive Coupling. VII.[1] A New Class of Acrylonitrile Oligomers

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Previous work on the electrolysis of acrylonitrile in aqueous quaternary ammonium salts under mildly alkaline conditions has been extended into the region of high acrylonitrile–water ratios. At very low water concentrations acetone-soluble, relatively low-melting polyacrylonitriles of average mol. wt. 600–1300 are formed. From electrolyses of catholytes of intermediate (but still low) water content there were isolated an acrylonitrile hydro trimer, 1,3,6-tricyanohexane, and a mixture of hydro tetramers, consisting of 1,3,6,8- and 1,3,5,8-tetracyanooctane. The structures of these new acrylonitrile oligomers were proved by conversion to and independent synthesis of the corresponding esters. The electrolytic hydropolymerization of acrylonitrile is viewed as proceeding from an initially formed α,α'-adiponitrile dianion.

There is a considerable literature[2] on the anionic polymerization of acrylonitrile (AN) by *chemical* means (*e.g.*, diethyl sodiomalonate, organolithium compounds, potassium alkoxides, and quaternary ammonium hydroxides[3]). In all cases, an alien anion, Z, which appears finally as an end group in the polymer, adds to AN to produce the initiating carbanion I.

$$\underset{}{Z\colon + CH_2{=}CHCN \longrightarrow} \underset{\text{I}}{(ZCH_2CHCN)^-}$$

Little has been published on the *electrolytic* carbanionic polymerization of AN.[4] Sr. M. Murphy and coworkers[7] observed polymer formation during polarography of AN in anhydrous dimethylformamide. They postulated that the initiating carbanion formed at the cathode is II, an entity also considered to participate in chain transfer during chemical anionic polymerization.[3]

$$\underset{\text{II}}{CH_2{=}\bar{C}\text{–}CN}$$

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[1] Paper VI: M. M. Baizer and J. D. Anderson, *J. Org. Chem.*, **30**, 1348 (1965).

[2] R. B. Cundall, D. D. Eley, and J. Worrall, *J. Polymer Sci.*, **58**, 869 (1962), and references cited therein.

[3] A. Zilkha, B. A. Feit, and M. Frankel, *ibid.*, **49**, 231 (1961).

[4] Since the preliminary announcement of our results[5] related work has been published by Funt and Williams[6a] and by Lazarov, Trifonov, and Vitanov.[6b]

[5] M. M. Baizer, *Tetrahedron Letters*, 973 (1963).

[6] (a) B. L. Funt and F. D. Williams, *J. Polymer Sci.*, *Pt. A*, **2**, 865 (1964); (b) S. Lazarov, A. Trifonov, and T. Vitanov, *Z. Physik. Chem.* (Leipzig), 221 (1964).

[7] M. Murphy, M. G. Carangelo, M. B. Ginaine, and M. C. Markham, *J. Polymer Sci.*, **54**, 107 (1961).

TABLE I

ELECTROLYTIC POLYMERIZATION OF ACRYLONITRILE

Expt. no.	Catholyte: Salt,[a] g.	AN, g.	Solvent (g.)	Water, g.	Temp., °C.	Amp.	Amp.-hr.	Solid PAN, g.	Av.[b] mol. wt.
1	25.0	23.1	DMF (82.3)	2.6	40	1.40–0.70	1.65	7.0	922
2	25.0	23.1	DMF (82.3)	4.0	40	1.40–0.70	1.50	3.9	902
3	25.0	23.1	DMF (82.3)	2.6	60	2.00–0.90	1.31	9.5	832
4	25.0	23.1	MeCN (82.3)	2.6	40–60	1.80–2.00	1.54	0	...
5	42.0	40.0	MeCN (132)	0	40	1.50–0.70	2.48	18.9	982
6	53.0	50.0	DMF (178)	5.6	40	1.00	1.5	21.7	929
7	27.0	108	None	2.7	40	1.00–1.50	2.65	None[c]	...
8	25.0	23.1[d]	DMF (82.3)	2.6[d]	40	1.00–1.80	2.80	12.0	734

[a] Tetraethylammonium *p*-toluenesulfonate. [b] Determined osmometrically in acetonitrile. [c] Liquid oligomers isolated. See Discussion below. [d] During the electrolysis an additional 10.7 ml. of AN and 2.6 ml. of water were added. Adiponitrile and hydro trimer were isolated as well as PAN.

Breitenbach, *et al.*,[8] have studied the electrolysis of dilute solutions of AN in anhydrous DMF using quaternary ammonium salts as supporting electrolytes. While they more recently[9] have favored a cathodically formed carbanion as the initiator of polymerization, they have not formulated the carbanion in question.

Electrolytic Polymerization of AN.—In a previous paper in this series[1] we mentioned that a polyacrylonitrile (PAN) was formed as by-product during the electrolytic reductive coupling of 8,8-diphenylbenzofulvene with acrylonitrile. The catholyte contained dimethylformamide (DMF), tetraethylammonium *p*-toluenesulfonate, and, in order to maintain homogeneity, only a small amount of water. In the latter respect it differed substantially from many other AN-containing catholytes which we had electrolyzed without obtaining polymers.[5] The polymerization was not inhibited by *p*-nitrosodimethylaniline and was not initiated in the absence of electric current. It therefore appeared to be an anionic polymerization initiated by the indene carbanion and, owing to the low concentration of water, not completely terminated in its earliest stages[1] (simple reductive coupling).

The above experiment was repeated in the absence of the indene. All other conditions were the same[10] except that now *ca.* -1.9 v. (s.c.e.) rather than -1.5 v. was necessary to start the cathodic reaction. As usual in our procedures, the electrolysis was run to only partial conversion. Amine was evolved from the catholyte; the pH was maintained at *ca.* 7.0–9.4[11] by dropwise addition of acetic acid. A polyacrylonitrile was formed. This experiment was replicated numerous times. The products were light to dark yellow solids[12] soluble in acetone, acetonitrile, DMF, and concentrated aqueous solutions of quaternary ammonium arylsulfonates (or alkylsulfates). They melted with decomposition over about a 20° range in the region 110–220°. Determination of the average molecular weight by the osmometric method (acetonitrile) gave values for the several samples of *ca.* 600–1300 (12–25 AN units).

Since our main objective at this time was to understand the factors which favored or hindered PAN formation, we carried out only a brief investigation of the effect of the reaction parameters upon the yield of polymer. The data are summarized in Table I.

Effect of Concentration of Water.—The yield of polymer was very sensitive to the quantity of water in the catholyte[13] (*cf.* expt. 2 *vs.* expt. 1).

Effect of Current Density.—One would anticipate that increasing the current density, by increasing the rate of initiation of new chains, would reduce the molecular weight of the polymer formed. This was only partially confirmed in our limited study (expt. 3 *vs.* expt. 2).

Effect of Organic Cosolvent.—Substituting an equal weight of acetonitrile for DMF (expt. 4) resulted in the formation of no solid PAN during electrolysis. When the water was omitted (expt. 5), solid polymer was obtained. It is known that acetonitrile is a proton donor.[14] It therefore appears that in the above polymerization both water and acetonitrile are contributing (protons) to the termination reaction.

Rate of Formation of PAN at Constant Current Density.—In an electrolysis similar to expt. 1, Table I, aliquots of the catholyte were removed every 30 min. and diluted with water. The precipitated polymer was removed by filtration, washed, and oven dried. The sharp decrease in the rate of polymerization coupled with the relative constancy of average molecular weight (Table II) suggests that with decreasing AN concentration (and increasing water–AN ratio) most polymer chains are being terminated at a stage before solid

TABLE II

RATE OF FORMATION OF POLYACRYLONITRILE

Time from start, min.	Total PAN, g.	Incremental PAN, g.	M.p., °C.	Mol. wt.[a]
30	7.46	7.46	134–160	703
60	16.7	9.25	134–160	688
90	22.4	5.75	106–137	670
120	26.9	4.45	104–140	591
150	27.3	0.40	142–164	674
180	29.0	1.70	142–164	886[b]

[a] Determined osmometrically in acetonitrile. [b] Gummy precipitate.

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(8) J. W. Breitenbach and Ch. Srna, *Pure Appl. Chem.*, **4**, 245 (1962).

(9) Breitenbach had originally suggested that cathodic discharge of a quaternary ammonium ion gives rise to a free-radical initiator. Since

$$R_4N^+ + e \longrightarrow R_4N\cdot \longrightarrow R_3N + R\cdot$$

tetraalkylammonium is discharged at a much more negative cathode potential (*ca.* -2.5 v. *vs.* s.c.e.) than is required for electron uptake by acrylonitrile (*ca.* -1.9 v.), it is unlikely that discharge of this type of cation is, as they asserted, involved in the polymerization process.

(10) It must be borne in mind that the extent of migration of water from the aqueous anolyte to the catholyte may vary from run to run and therefore the water content of the catholyte is not readily duplicated.

(11) M. M. Baizer, *J. Electrochem. Soc.*, **111**, 215 (1964). Under these conditions cyanoethylation of water is negligible; hydroxide-initiated polymerization therefore appears to be excluded.

(12) The color of anionic PAN has been discussed by Cundall, *et al.*[3]

(13) Breitenbach[8] had noted a similar phenomenon.

(14) S. Wawzonek, E. W. Blaha, R. Berkey, and M. E. Runner, *J. Electrochem. Soc.*, **102**, 235 (1955).

TABLE III

HYDROGENATIONS OF 1,3,6-TRICYANOHEXANE

	Charge			Products			
Run	VII, g.	Ammonia, g.	Catalyst (g.)	XI, g.	X, g.	Polyamine, g.	Time, hr.
1	30.0	107.0	Pelleted Co (10.2)	11.7	...	...	6
2	30.0	106.0	Raney Co (2.0) commercial	14.6	...	...	7
3	28.1	60.0	Raney Ni (3.0) commercial	Decomposed on distillation			5.5
4	25.0	55.0	Raney Co (3.0) W-4	16.0	5.0	2.4	22
5	30.0	60.0	Raney Co (3.0) W-4	16.7	6.3	5.4	23
6	40.0	70.0	Raney Co (3.0) W-4	19.6	14.5	5.0	20
7	40.0	70.0	Raney Co (3.0) W-4	21.6	14.1	5.0	21
8	100.0	200.0	Raney Co (10.0) W-4	65.8	27.6	10.0	7
9	100.0	200.0	Raney Co (10.0) W-4	54.8	36.2	9.2	8

polymer is formed. Liquid oligomers were indeed obtained, *e.g.*, expt. 8, Table I.

Genesis of the Electrolytic Polyacrylonitrile.—Polarographic reduction of AN indicates a single two-electron step in aqueous or nonaqueous medium.[6b] In the absence of experimental evidence that there is a discontinuity in the mode of reduction of AN in changing the proton-donor concentration we may rationalize the formation of the entire range of AN electroreduction products on the basis of the previously proposed[5] dicarbanion III. In very dilute solutions of AN, pro-

$$\mathrm{(CH_2CHCN)^{-2}}$$

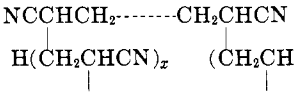
III

pionitrile is the principal final product. As the concentration of AN is increased, III reacts with AN rather than with water so that the coupled carbanions IV and/or IVa are formed.[15] The latter upon reaction with water yields adiponitrile. When the AN–water ratio

$$\mathrm{(CNCHCH_2CH_2CHCN)^{-2}} \qquad \mathrm{(CNCH_2CH_2CH_2CHCN)^{-}}$$

IV IVa

is very high, as in the polymerization experiments described above, the carbanions IV and IVa may undergo a series of successive Michael reactions[16] with several AN molecules in sequence before the growing carbanion chain terminates by displacing OH^- from water. On this basis, the structure of the polymers[17] would be V in which x (or y) may be zero and $x + y$ equals *ca.* 10–23.



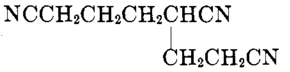
$$\mathrm{NC}\underset{\substack{|\\ \mathrm{H(CH_2CHCN)}_x\\ |}}{\mathrm{C}}\mathrm{HCH_2}\text{--------}\mathrm{CH_2}\underset{\substack{|\\ \mathrm{(CH_2CHCN)}_y\mathrm{H}\\ |}}{\mathrm{C}}\mathrm{HCN}$$

V

Partial support for formulation V was found in the isolation and proof of structure of two of the "missing links" between adiponitrile (V, x and $y = 0$) and our PAN (V, $x + y = ca.$ 10–23). These intermediates, high-boiling viscous oils, are members of a new class of AN oligomers.[18] They were obtained from several sources. In an electrolysis of AN in 97% dimethylformamide, AN and water were added dropwise to the catholyte as the reaction proceeded[19] (expt. 8, Table I). In addition to PAN a liquid fraction, b.p. 134–178° (0.2 mm.), was isolated. An electrolysis in 91% tetraethylammonium *p*-toluenesulfonate without cosolvent yielded no PAN and only the high-boiling oil (expt. 7, Table I). Finally the residues from many electrolytic adiponitrile preparations furnished additional crude by-product.

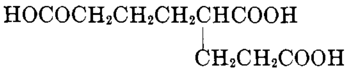
The oils were separated by simple distillation into two components: VII, a light yellow slightly viscous liquid, b.p. 186–200° (0.2 mm.), and VIII, an amber very viscous liquid, b.p. 264–288° (0.05–0.18 mm.). A dark tarry residue was not further investigated.

Acrylonitrile Hydro Trimer.—Elemental and molecular weight determinations of crude VII pointed to its formulation as an AN hydro trimer.[20] Hydrolysis of VII with concentrated HCl (or better, with 10% NaOH) yielded an acid, m.p. 112°. The melting point of the known acid IX is reported[21] to be 111 or 112°. A sam-



$$\mathrm{NCCH_2CH_2CH_2}\underset{\substack{|\\ \mathrm{CH_2CH_2CN}}}{\mathrm{C}}\mathrm{HCN}$$

VII



$$\mathrm{HOCOCH_2CH_2CH_2}\underset{\substack{|\\ \mathrm{CH_2CH_2COOH}}}{\mathrm{C}}\mathrm{HCOOH}$$

IX

ple of IX prepared by the novel route given below showed no melting point depression when admixed with acid prepared from VII; VII is therefore 1,3,6-tricyanohexane.

$$\mathrm{CN(CH_2)_3CH(COOC_2H_5)_2} \xrightarrow[\text{KOH–MeOH}]{\text{AN}} \mathrm{CN(CH_2)_3C(COOC_2H_5)_2(CH_2CH_2CN)} \xrightarrow[\Delta]{\text{concd. HCl}} \mathrm{IX}$$

The triethyl ester of IX was also obtained, in the electrolysis of ethyl acrylate in the presence of a limited amount of water.

Catalytic hydrogenation of the new trinitrile VII in a rocking autoclave under 5000 p.s.i. and 150° in the presence of ammonia and Raney cobalt catalyst yielded two characterized products in addition to polyamine residues. The lower boiling amine product was identified as 3-(4-aminobutyl)piperidine (X)[22] on the basis of agreement of the melting points and analyses of the dihydrochloride and di-*p*-toluenesulfonamide with the

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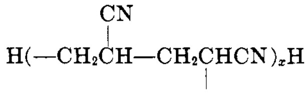
[15] Intermediate IV has now been postulated by other workers.[6]

[16] O. C. Bockman and C. Schuerch [*J. Polymer Sci. Pt. B*, **1**, 145 (1963)] have recently discussed anionic polymerizations *via* the Michael reaction.

[17] This structure differs from that of PAN formed by free-radical initiation insofar as V contains one six-carbon chain (absent in VI) and may be considered to be derived from the α,α'-dianion of adiponitrile.



$$\mathrm{H(-CH_2}\overset{\substack{\mathrm{CN}\\ |}}{\mathrm{C}}\mathrm{H-CH_2}\underset{|}{\mathrm{C}}\mathrm{HCN)}_x\mathrm{H}$$

VI

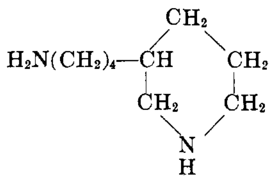
[18] H. Zahn and P. Schäfer [*Makromol. Chem.*, **30**, 225 (1959); *Chem. Ber.*, **92**, 735 (1959)], H. Zahn and G. B. Gleitsmann [*Angew. Chem.*, **75**, 772 (1963)], and T. Takata, H. Ishii, J. Mishiyama, and M. Taniyama [*Chem. High Polymers* (Tokyo), **18**, 235 (1961)] have all described the synthesis of several AN oligomers related to free-radical PAN, VI.

[19] The purpose of this procedure was to maintain the same current density throughout the run. In the usual PAN runs the current density had tended to drop as the AN was depleted.

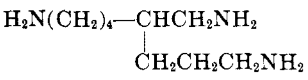
[20] The infrared spectrum showed the presence of a minor amount of $CONH_2$; the analyses therefore deviated from the theoretical.

[21] S. Dev and C. Rai, *J. Indian Chem. Soc.*, **34**, 266 (1957); M. Lamant, *Compt. rend.*, **242**, 380 (1956).

[22] P. G. Haines, A. Eisner, and C. F. Woodward, *J. Am. Chem. Soc.*, **67**, 1258 (1945).



X



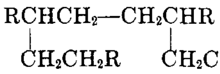
XI

$H_2N(CH_2)_4-\underset{\displaystyle CH_2CH_2CH_2NH_2}{CHCH_2NH_2}$

reported values. The higher boiling product (XI) was characterized by analysis of the free base and its trioxalate and tribenzoyl derivatives (X was also prepared by deaminative ring closure of XI). A summary of the hydrogenation experiments is given in Table III.

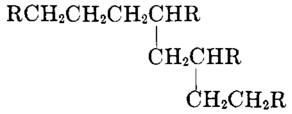
Acetylation of X followed by dehydrogenation of the unisolated diacetyl derivative with 10% palladium on carbon yielded the pyridine which was directly oxidized by concentrated nitric acid to nicotinic acid.[23] This sequence constitutes a formal route from acrylonitrile to nicotinic acid.

Acrylonitrile Hydro Tetramers.—Analytical evidence indicated that VIII was an AN hydro tetramer. Two formulations (XII and XIII, $R = CN$) are consistent with our postulated mechanism of formation. To minimize synthetic difficulties, the tetraethyl esters corresponding to XII and XIII ($R = COOC_2H_5$) were independently prepared and compared with the esters obtained from VIII.



XII

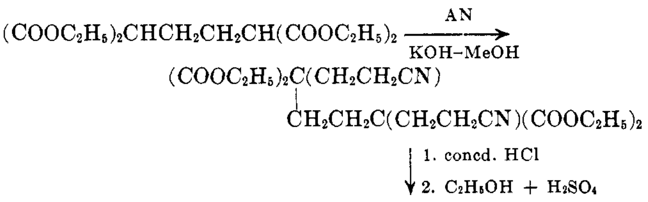
$\underset{\displaystyle CH_2CH_2R}{RCH}CH_2-CH_2\underset{\displaystyle CH_2CH_2R}{CHR}$



XIII

$RCH_2CH_2CH_2\underset{\underset{\displaystyle CH_2CH_2R}{\displaystyle CH_2CHR}}{CHR}$

The synthesis of XII ($R = COOC_2H_5$) from tetraethyl 1,1,4,4-butanetetracarboxylate according to the scheme shown offered no difficulties. The disastereoisomeric products, b.p. 166–184° (0.08–0.10 mm.), were not separated before further examination.



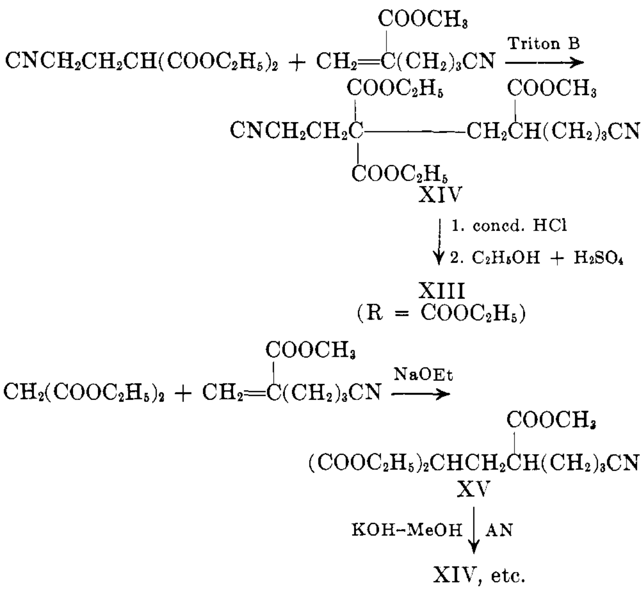
$$(COOC_2H_5)_2CHCH_2CH_2CH(COOC_2H_5)_2 \xrightarrow[KOH-MeOH]{AN} (COOC_2H_5)_2C(CH_2CH_2CN)\text{—}CH_2CH_2C(CH_2CH_2CN)(COOC_2H_5)_2 \xrightarrow[2.\ C_2H_5OH\ +\ H_2SO_4]{1.\ concd.\ HCl}$$

XII
($R = COOC_2H_5$)

Projected syntheses of XIII ($R = COOC_2H_5$) from intermediates described by Lukes[24] were unsuccessful. The two sequences summarized below, however, were successful. Again the diastereoisomeric esters (XIII, $R = COOC_2H_5$) were not separated, b.p. 172–182° (0.25 mm.).

Both n.m.r. and v.p.c. examination of the tetraethyl esters prepared from VIII showed that they were mixtures of XII and XIII ($R = COOC_2H_5$) and contained no other constituent.

Electrolytic Degradation of Our PAN.—Attempts to prepare AN oligomers by thermal degradation of ordinary PAN have not been very promising.[25] Since our lower molecular weight PAN is more tractable and since even only slight reversal of the Michael reactions by which it was formed would yield an electroreducible α,β-unsaturated nitrile subsequently inert to further reaction,[26] an electrochemical degradation of our PAN was attempted. Electrolysis of PAN (av. mol. wt. 965) in aqueous DMF containing tetraethylammonium *p*-toluenesulfonate proceeded at −1.75 to −1.90 v. (*vs.* s.c.e.). Gas was continuously evolved at the cathode. Of the polymer recovered *ca.* 90% was acetone soluble and had a molecular weight of 784; the remainder was insoluble in acetone or acetonitrile (amides?).



$$CNCH_2CH_2CH(COOC_2H_5)_2 + CH_2{=}\overset{\displaystyle COOCH_3}{C}(CH_2)_3CN \xrightarrow{\text{Triton B}} CNCH_2CH_2\underset{\displaystyle COOC_2H_5}{\overset{\displaystyle COOC_2H_5}{C}}\text{——}CH_2\overset{\displaystyle COOCH_3}{CH}(CH_2)_3CN$$

XIV

$$\xrightarrow[2.\ C_2H_5OH\ +\ H_2SO_4]{1.\ concd.\ HCl} \text{XIII } (R = COOC_2H_5)$$

$$CH_2(COOC_2H_5)_2 + CH_2{=}\overset{\displaystyle COOCH_3}{C}(CH_2)_3CN \xrightarrow{NaOEt} (COOC_2H_5)_2CHCH_2\overset{\displaystyle COOCH_3}{CH}(CH_2)_3CN$$

XV

$$\xrightarrow[AN]{KOH-MeOH} \text{XIV, etc.}$$

Experimental[27]

Preparation of Polyacrylonitrile.—The cathode chamber of the electrolytic cell previously described[12] was charged with 23.1 g. of AN, 25.0 g. of tetraethylammonium *p*-toluenesulfonate, 82.3 g. of DMF, and 2.6 g. of water. The anolyte contained 20 ml. of 60% quaternary salt solution. The electrolysis was carried out at 40°, a cathode voltage of −1.89 to −1.75 v. (s.c.e.) and a gradually decreasing amperage of 1.40 to 0.70 amp. Acetic acid (1.90 ml.) was added dropwise to maintain the catholyte slightly alkaline. After 140 min. (1.65 amp.-hr.) the catholyte was transferred to a separatory funnel, the mercury was separated, and the solution was allowed to run slowly with stirring into 300 ml. of water. The light yellow PAN was removed by filtration and dried; 7.0 g. The average molecular weight (osmometrically, acetonitrile solvent) was 922 ± 3%.

Variations in this procedure are summarized in Table I.

Rate of Formation of PAN.—The catholyte contained 38.6 g. of AN, 41.8 g. of the above salt, 137.4 g. of DMF, and 3.0 g. of water. The anolyte was 45 ml. of 61% methyltri-*n*-butylammonium *p*-toluenesulfonate. The electrolysis was conducted at 40° and a constant amperage of 1.50 amp. A 5.0-ml. portion of the catholyte was removed every 30 min. and diluted with 15 ml. of water. The polymer was removed by filtration, washed, and oven dried. The results are summarized in Table II.

Hydrolysis of VII. A. By Acid.—A 7.6-g. sample of VII was heated under reflux with 25 ml. of concentrated HCl for 19 hr. Then 10 ml. more of acid was added[28] and reflux was continued for 3 hr. The mixture was poured onto ice and made slightly alkaline with potassium carbonate. The solution was extracted once with ether; the extract was discarded. The acidified aqueous solution was now extracted with six 25-ml. portions of ether. The combined extracts were washed with water, dried over calcium sulfate, and freed of solvent. The light

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[23] S. M. McElvain, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 385.

[24] R. Lukes, *et al.*, *Chem. Listy*, **52**, 682 (1958); *Chem. Abstr.*, **52**, 13636*h* (1958).

[25] H. Zahn and P. Schäfer, ref. 18.

[26] In the presence of a substantial concentration of water the slowly formed α,β-unsaturated nitrile fragment would have more opportunity to yield its dihydro product than to undergo hydrodimerization.

[27] Boiling points are uncorrected. All AN contained *p*-nitrosodimethylaniline as stabilizer.

[28] *Cf.* Zahn and Schäfer's procedures, ref. 18.

amber oily residue crystallized on trituration with a mixture of acetone and methylene chloride. The white crystals were removed by filtration, washed with methylene chloride, and dried at 75°; m.p. 112°.

Anal. Calcd. for $C_9H_{14}O_6$: C, 49.54; H, 6.47; neut. equiv., 72.7. Found: C, 49.40; H, 6.55; neut. equiv., 73.2.

B. **By Alkali.**—To a solution of 46.8 g. (1.17 moles) of sodium hydroxide in 470 ml. of water was added gradually with stirring 40.0 g. (0.25 mole) of VII. The mixture was heated under reflux for 60 hr., then cooled, and acidified with HCl. The salt was removed by filtration and the filtrate was extracted continuously with ether for *ca.* 60 hr. Evaporation of the ether left 43.9 g. (80%) of the triacid, m.p. 112–114°.

Synthesis of 4-Carboxysuberic Acid (IX).—To a stirred solution of 24.0 g. (0.106 mole) of diethyl α-(3-cyanopropyl) malonate[29] [b.p. 132–138° (0.30–0.35 mm., $n^{25}\mathrm{D}$ 1.4375] in 50 ml. of *t*-butyl alcohol at room temperature was added several drops of 30% potassium hydroxide in methanol. Acrylonitrile (6.4 g., 0.12 mole) was added dropwise in 30 min. The temperature rose spontaneously to 33°. When it dropped to 29° the mixture was heated to and held at 35° for 100 min. A 1:4 HCl solution added to destroy the catalyst simultaneously caused precipitation of solid product which was removed by filtration, thoroughly washed with water, and vacuum dried; 25.2 g., m.p. 66–66.5°. From the filtrate there was obtained by extraction with methylene chloride, removal of the solvent, and crystallization of the residue from *t*-butyl alcohol an additional 2.9 g. of product. The total yield of diethyl α-(3-cyanopropyl)-α-(2-cyanoethyl)malonate was 94.5%. Before analysis a sample was recrystallized from *t*-butyl alcohol; m.p. 67–67.5°.

Anal. Calcd. for $C_{14}H_{20}N_2O_4$: C, 59.98; H, 7.18; N, 9.99. Found: C, 60.20; H, 7.23; N, 9.70.

A mixture of 10 g. of the above ester and 30 ml. of concentrated HCl was heated under reflux for 17 hr. Two more portions of concentrated HCl (5 and 15 ml.) were added in the course of the next 24 hr. The excess HCl was then removed *in vacuo*. The residue was powdered and triturated in several portions with a total of 200 ml. of dry ether. The ether residue on trituration with methylene chloride–acetone yielded white crystals of IX, m.p. 111°. There was no depression in melting point when the triacid from VII was added.

Catalytic Hydrogenation of VII.—The trinitrile and catalyst were charged to a 300-ml. or 1000-ml. bomb (as appropriate to sample size). The bomb was cooled in Dry Ice–acetone and evacuated, and ammonia was distilled in. Hydrogen was introduced to *ca.* 1000 p.s.i., the bomb was rocked and heated to 150°, and additional hydrogen was used to bring the pressure to 5000 p.s.i. After uptake was no longer apparent, maximum pressure was restored, heating was continued, and the rocking was allowed to proceed overnight. The contents were filtered and the filtrate was fractionated through an 18-in. narrow-bore Vigreux column: (1) 3-(4-aminobutyl)piperidine (X), b.p. 67° (0.1 mm.), $n^{25}\mathrm{D}$ 1.4820, solidifying in the receiver; (2) 4-aminomethyl-1,8-diaminooctane (XI), b.p. 100–102° (0.2 mm.), $n^{25}\mathrm{D}$ 1.4858; and (3) polymeric residue. The triamine XI was analyzed.

Anal. Calcd. for $C_9H_{23}N_3$: C, 62.43; H, 13.29; N, 24.28. Found: C, 62.13; H, 13.59; N, 24.31.

A sample was treated with excess oxalic acid in ethanol. The **trioxalate** was recrystallized from aqueous ethanol; m.p. 132–134°.

Anal. Calcd. for $C_{15}H_{29}N_3O_{12}$: C, 40.63; H, 6.55; N, 9.48. Found: C, 40.66; H, 6.59; N, 9.46.

The tribenzoyl derivative was prepared by a standard procedure and recrystallized from hexane; m.p. 143–145°.

Anal. Calcd. for $C_{30}H_{35}N_3O_3$: C, 74.23; H, 7.22; N, 8.66. Found: C, 74.68; H, 7.67; N, 8.46.

Conversion of XI to X.—A mixture of 21.0 g. of XI and 3.0 g. of W-4 Raney cobalt was charged to a 300-ml. bomb and 20.0 g. of ammonia was introduced as above. The vessel was pressured with hydrogen and heated to 150°. The bomb was rocked for 3 hr. at 3750 p.s.i. Work-up yielded 4.2 g. of X, 12.5 g. of unchanged XI, and 3.1 g. of polyamine.

Conversion of X to Nicotinic Acid.—To 6.5 g. (0.042 mole) of X in 10 ml. of dry benzene was gradually added 9.1 g. (*ca.* 0.084 mole) of acetic anhydride.[30] The exothermic reaction brought the mixture to reflux. After heating 1 hr. the volatile materials were removed on the water bath by vacuum. The residual sirup was dissolved in benzene, washed with sodium bicarbonate solution and then water, and dried. Removal of the solvent and evacuation of the residue at 50° left 9.0 g. (90% of crude diacetyl derivative) of sirup. The crude product was mixed with 1.0 g. of 10% palladium on charcoal and heated to 272° (internal temperature) in the course of 4.5 hr. The mixture was cooled and another charge of catalyst was added; it was then reheated to 250° in the course of 1.2 hr. A total of 1135 ml. of hydrogen was collected over water (theory, 1790 ml.). The pyridine intermediate was leached from the catalyst mass by means of methylene chloride. Concentration of the extracts yielded 6.9 g. (theory 7.2 g.). The residue was oxidized with 75 ml. of concentrated nitric acid[23] as in the oxidation of nicotine. The nicotinic acid nitrate, obtained in two crops, weighed *ca.* 2 g., m.p. 187–188°. A sample was converted to the free acid which, after recrystallization from alcohol, melted at 232–236°. An infrared spectrum (Nujol mull) showed this product to be identical with an authentic sample of nicotinic acid.

Hydrolysis of Acrylonitrile Hydro Tetramers (VIII) and Esterification of the Resultant Acids. A.—A mixture of 10 ml. of concentrated HCl and 2.6 g. of VIII was heated under reflux for 2 days with intermediate addition of 4.5 ml. more of acid. The excess HCl was removed *in vacuo*. The residue was triturated numerous times with dry ether. The ether residue solidified on trituration with methylene chloride–acetone. The solid product was recrystallized from ethyl acetate with charcoal: first crop, m.p. 141–158°; second crop, m.p. 136–143°. A sample of the first crop was analyzed.

Anal. Calcd. for $C_{12}H_{18}O_8$: C, 49.65; H, 6.25; neut. equiv., 72.5. Found: C, 49.52; H, 6.06; neut. equiv., 74.

A mixture of the first and second crops (0.46 g.) was suspended in 5 ml. of absolute ethanol. Two drops of concentrated sulfuric acid was added and the mixture was heated under reflux 24 hr. The mixture was poured onto ice, made alkaline with sodium bicarbonate, and extracted with methylene chloride (three portions). The extracts were washed, dried, and freed of solvent. The residual ester (*ca.* 0.5 g.) was distilled; b.p. 174–198° (0.10–0.15 mm.) (superheating), $n^{25}\mathrm{D}$ 1.4471.

Anal. Calcd. for $C_{20}H_{34}O_8$: C, 59.68; H, 8.51. Found: C, 59.33; H, 8.42.

B.—A 13.2-g. sample of VIII was hydrolyzed as above. To the crude acids in 100 ml. of absolute alcohol was added 3 ml. of concentrated sulfuric acid. The mixture was heated under reflux for 22 hr. The ester fraction, isolated in the usual way, was fractionated through a 2-ft. jacketed Vigreux column. The fraction (9.4 g.) boiling at 177–193° (0.25 mm.) was redistilled and the portion boiling at 172–181° (0.15–0.20 mm.) was purified by passage through activated alumina and analyzed; $n^{25}\mathrm{D}$ 1.4498.

Anal. Found: C, 59.72; H, 8.54.

Synthesis of Tetraethyl 1,3,6,8-Octanetetracarboxylate (XII, R = $COOC_2H_5$).—To a stirred solution of 17.9 g. (0.0518 mole) of tetraethyl 1,1,4,4-butanetetracarboxylate[31] in 40 ml. of *t*-butyl alcohol containing a few drops of 30% methanolic potassium hydroxide, 6.0 g. of acrylonitrile was added dropwise in 35 min. The temperature rose spontaneously (maximum 36°) and crystals deposited after the first 22 min. When the temperature dropped to 30°, the mixture was heated at 35° for 3 hr. It was then chilled to 25°, the catalyst was destroyed by addition of 1:4 HCl, and the mixture was poured into 100 ml. of water. The solid was removed by filtration, washed with water, and dried; 20.3 g. (87%), m.p. 90–91°. From the filtrate there was obtained after extraction, etc., 2.3 g. of oil which did not crystallize. Before analysis a sample of the solid, tetraethyl 1,4-bis(2-cyanoethyl)-1,1,4,4-butanetetracarboxylate, was recrystallized from *t*-butyl alcohol; m.p. 93–94°.

Anal. Calcd. for $C_{22}H_{32}N_2O_8$: C, 58.39; H, 7.13; N, 6.19. Found: C, 58.24; H, 7.17; N, 6.15.

The 20.3 g. of cyano ester was hydrolyzed with concentrated HCl as in the examples above. After removal of the excess acid, the residue was extracted in a Soxhlet with dry ether for several days yielding 4.1 g. of acid. Trituration of the original cake

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[29] P. Olynyk, *et al.*, *J. Org. Chem.*, **13**, 465 (1948).

[30] Attempts to dehydrogenate X without prior acetylation led to sirups which on oxidation with nitric acid or permanganate did not yield nicotinic acid.

[31] C. S. Marvel and R. D. Vest, *J. Am. Chem. Soc.*, **81**, 985 (1959).

with acetone yielded an additional 3.7 g. of acid. Finally, washing the cake with cold water left 5.8 g. of acid undissolved. The combined crops of acid (13.6 g.) were esterified with ethanol-sulfuric acid. The crude esters (14.5 g., 80% based on cyanoester) were fractionated and the major fraction [9.0 g., b.p. 166–184° (0.08–0.10 mm.), n^{25}D 1.4480] was analyzed.

Anal. Calcd. for $C_{20}H_{34}O_8$: C, 59.68; H, 8.51. Found: C, 59.41; H, 8.43.

Preparation of 4,4-Bis(ethoxycarbonyl)-6-methoxycarbonylsebaconitrile (XIV).—To a stirred solution of 21.3 g. (0.10 mole) of diethyl α-(2-cyanoethyl)malonate[32] in 20 ml. of *t*-butyl alcohol at 18° was added 2 ml. of Triton B. The temperature was allowed to rise to 25°. A solution of 15.3 g. (0.10 mole) of methyl α-(3-cyanopropyl)acrylate[33] in 5 ml. of *t*-butyl alcohol was added in 17 min. The temperature rose to 27°. For the next 75 min. the mixture was warmed at 35° while two additional portions of catalyst were added. After an additional 90 min., the mixture was cooled to 15° and 1:4 HCl was added dropwise to destroy the catalyst. The diluted mixture was extracted with three 30-ml. portions of methylene chloride. The extracts were washed with sodium bicarbonate solution and water, and then dried over calcium sulfate. After the solvent was removed by distillation, the residual liquid was fractionally distilled; the portion (14.6 g., 40%) boiling at 200–217° (0.3–0.4 mm.), n^{25}D 1.4600, was analyzed.

Anal. Calcd. for $C_{18}H_{26}N_2O_6$: C, 59.00; H, 7.13; N, 7.65. Found: C, 58.98; H, 7.14; N, 7.23.

Conversion of XIV to XIII (R = $COOC_2H_5$).—Ten grams of XIV was hydrolyzed with concentrated HCl by the procedures described above. The crude acids (8.1 g.) were esterified with ethanol-sulfuric acid. The crude esters (9.2 g.) were vacuum distilled. The major fraction (4.8 g.), b.p. 180–182° (0.3–0.25 mm.), n^{25}D 1.4470, a pale yellow liquid, was analyzed.

Anal. Calcd. for $C_{20}H_{34}O_8$: C, 59.68; H, 8.51. Found: C, 59.46; H, 8.21.

Preparation of Diethyl α-(3-Methoxycarbonyl-6-cyano)hexylmalonate (XV).—To a solution of 0.5 g. of sodium in 30 ml. of absolute ethanol at 20° was added with stirring 16.0 g. (0.10 mole) of diethyl malonate. The temperature was allowed to rise to 24.5° and 15.3 g. (0.10 mole) of methyl α-(3-cyanopropyl)-acrylate[33] was added in 13 min. The temperature rose to a maximum of 32°. Stirring was continued for 4 hr. while the temperature slowly dropped to 26°. The mixture was cooled to 15°, made slightly acid with acetic acid, and diluted with 150 ml. of water. It was extracted with three 50-ml. portions of methylene chloride. The extracts were washed, dried, and fractionated. The portion (16.0 g., 51%) boiling at 162–175° (0.15–0.20 mm.), n^{25}D 1.4485, was collected as XV.

Anal. Calcd. for $C_{15}H_{23}NO_6$: C, 57.49; H, 7.40; N, 4.47. Found: C, 57.50; H, 7.69; N, 3.45.[34]

Conversion of XV to XIV.—A solution of 16.0 g. (0.051 mole) of XV in 30 ml. of *t*-butyl alcohol was cyanoethylated as in examples above using a few drops of 30% methanolic potassium hydroxide as catalyst. The crude product was fractionated and the portion (13.3 g., 71.3%) boiling at 196–210° (0.2–0.3 mm.), n^{52}D 1.4600, was collected as XIV.

Anal. Calcd. for $C_{18}H_{26}N_2O_6$: C, 59.00; H, 7.13; N, 7.65. Found: C, 58.73; H, 7.25; N, 5.61.[34]

Electrolytic Degradation of "Low Molecular Weight" PAN.—The catholyte contained 23.2 g. of tetraethylammonium *p*-toluenesulfonate, 23.2 g. of PAN of average mol. wt. 965, 23.2 g. of water, and 78.7 g. of DMF. The anolyte was a DMF–water solution of the same salt. Electrolysis was at −1.75 to −1.90 v. (s.c.e.); the amperage was *ca.* 1.0 amp., total 5.57 amp.-hr. As the electrolysis proceeded water was added dropwise from time to time to the catholyte. The temperature was 55°. The mercury was separated and the solution was added with stirring to 500 ml. of ice and water. After standing overnight, the solid was removed by filtration, dried on the funnel, and washed with methylene chloride. The polymer was suspended in 400 ml. of acetone and filtered and the filtrate was added slowly with stirring to 1000 ml. of water. The reprecipitated polymer, 18.0 g. after drying, had an average molecular weight (osmometrically in acetonitrile) of 784 ± 3%. The acetone-insoluble material was dissolved in DMF and reprecipitated with water; 2.1 g. of tan-orange solid.

Electrolytic Preparation of the Triethyl Ester of IX.—The catholyte contained 73.0 g. of stabilized ethyl acrylate, 41.8 g. of tetraethylammonium *p*-toluenesulfonate, 137 g. of DMF, and 3.0 g. of water. The anolyte was 50 ml. of a 60% aqueous solution of the above salt. Electrolysis proceeded at 30° and 2.0 amp., total 8.3 amp-hr. The pH was controlled as usual. The catholyte, after separation of the mercury, was diluted with 300 ml. of water and extracted with six 50-ml. portions of methylene chloride. The extracts were washed, dried, and fractionated. After removal of excess starting material and of diethyl adipate,[35] the fraction (7.9 g.) boiling at 132–205° (0.55–0.5 mm.) was collected and refractionated. The product (5.0 g.) boiling at 114–122° (0.03–0.04 mm.), n^{25}D 1.4565, was triethyl 1,4,6-hexanetricarboxylate.[36]

Anal. Calcd. for $C_{15}H_{26}O_6$: C, 59.91; H, 8.67; mol. wt., 302. Found: C, 60.03; H, 8.54; mol. wt., 311.

A 0.4-g. sample of this triester upon hydrolysis with concentrated HCl yielded 0.2 g. of IX, m.p. 112–114°.

Acknowledgment.—All instrumental analyses were performed by Donald Beasecker's group. We are grateful to James Downing for the preparation of some of the starting materials.

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[32] N. F. Albertson and J. L. Fillman, *J. Am. Chem. Soc.*, **71**, 2818 (1949).

[33] C. J. Albisetti, *et al.*, *ibid.*, **78**, 472 (1956).

[34] Nitrogen analyses were inexplicably low.

[35] M. M. Baizer and J. D. Anderson, *J. Electrochem. Soc.*, **111**, 223 (1964).

[36] S. Dev and C. Rai[21] report the following constants for this ester: b.p. 185–188 (3 mm.), n^{22}D 1.4400.