The Reactions of Dinitriles and their Derivatives with Formaldehyde[1]
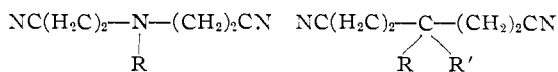
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The acid-catalyzed reaction of formaldehyde with dinitriles to produce polyamides and, specifically, the effect of centers of decreasing basicity in the nitrile was studied. It was found that dinitriles containing basic centers failed to polymerize with formaldehyde.

The existence of a reaction between nitriles and formaldehyde has been known for some time, but not until recently has it been thoroughly and systematically investigated. In an acidic medium, nitriles react with formaldehyde (in the ratio of two to one) to yield methylenebisamides or their homologs.[2-4] With equimolar amounts of the dinitrile and formaldehyde, the reaction takes a different course to yield perhydrotriazine derivatives in excellent yields.[5-7] Recently Magat[8] and his co-workers published a series of papers dealing with the acid-catalyzed reaction of nitriles with formaldehyde and the preparation of polyamides from dinitriles and formaldehyde. These publications were slightly predated by Mowry and Ringwald's[9] study of the reaction of azelaonitrile with formaldehyde which yielded a polyamide.

The vast majority of the work reported in the literature deals with the interaction of formaldehyde and unsubstituted dinitriles. Substituted dinitriles like 9,9-bis-(β-cyanoethyl)-fluorene, 2-methyladiponitrile and β,β'-dicyanodiethyl ether also gave polymers with formaldehyde, but in very low yields. Therefore, it seemed important to determine the scope and limitations of this method of polyamide formation.

Mowry[9] proposed a carbonium ion mechanism for the reaction; the first step involved the attack on the dinitrile by a methylolcarbonium ion ($^+CH_2$-OH) formed by addition of a proton to formaldehyde. It was therefore of interest to investigate whether the presence of a basic (in the Lewis sense) center in the dinitrile would alter the course of the reaction.

$$NC(H_2C)_2\text{—}N\text{—}(CH_2)_2CN \qquad NC(H_2C)_2\text{—}C\text{—}(CH_2)_2CN$$
$$\qquad\qquad | \qquad\qquad\qquad\qquad\qquad /\ \backslash$$
$$\qquad\qquad R \qquad\qquad\qquad\qquad\qquad R\quad R'$$

I, R = H
II, R = H_3CCO^-
III, R = $C_6H_5CH_2^-$
IV, R = CF_3CO^-
V, R = $C_6H_5CO^-$
VI, R = $C_6H_5SO_2^-$
VII, R = $(O_2N)_2C_6H_3CO^-$
VIII, R = CH_3, R' = H_3CCO^-
IX, R = CH_3CO^-, R' = H_3CCO^-
X, R = $C_2H_5CO_2^-$, R = $C_2H_5CO_2^-$
XI, R = NO_2, R' = NO_2

(1) Abstracted from a thesis by Stanley M. Pier, submitted to the faculty of Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1952.

(2) E. Hepp and G. Spiess, Ber., 9, 1424 (1876).

(3) R. F. Batt and D. Woodcock, J. Chem. Soc., 2322 (1948).

(4) R. L. Wain, Ann. Rept. Res. Sta. Long Ashton, 126 (1944).

(5) T. L. Gresham and T. R. Steadman, This Journal, 71, 1872 (1949).

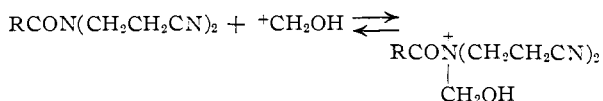(6) M. A. Gradsten and M. W. Pollock, ibid., 70, 3079 (1948).

(7) R. Wegler and A. Ballauf, Chem. Ber., 81, 527 (1948).

(8) E. E. Magat, et.al., This Journal, 73, 1028, 1031 (1951).

(9) D. T. Mowry and E. L. Ringwald, ibid., 72, 4439 (1950).

In a recent patent[10] it is claimed that polyamides were obtained from compound I and its derivatives containing basic centers. However, no elemental analyses or physical data are given for these polymers and extensive efforts in this Laboratory failed to produce polyamides from compounds I, II[11] or III. These compounds may fail to undergo polymerization because in the strongly acidic reaction medium a proton could attach to the basic nitrogen atom, thus imparting a positive over-all charge to the dinitrile. The attack of a methylolcarbonium ion on the dinitrile would then become difficult or impossible. A possible initial reaction of the methylcarbonium ion with the basic nitrogen would also give rise to an ammonium type ion which of course is similar to the one mentioned above.

$$RCON(CH_2CH_2CN)_2 + {}^+CH_2OH \rightleftharpoons$$
$$\qquad\qquad\qquad\qquad RCO\overset{+}{N}(CH_2CH_2CN)_2$$
$$\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad\qquad CH_2OH$$

A possible reason for the failure of II to polymerize with formaldehyde could have been the hydrolysis of the acetyl group in the acidic medium to give I. However, a Duclaux number type determination established that the acetyl group was not lost in the highly acidic medium.

If the failure to polymerize is due to the formation of a positive ion, it should be possible to recover a basic dinitrile from the reaction mixture. This was carried out in the case of compound III, of which 80% was recovered after treatment with formaldehyde and sulfuric acid.

To test further whether the basic center in II interfered with the polyamide formation, the polymerization was studied with compounds IV, V, VI and VII in which the basicity of the amide nitrogens are very much decreased because of inductive and resonance effects of the various groups. No difficulties were encountered in the polymerization with formaldehyde, and the polymers obtained are shown in Table I.

To gain further information regarding the utility of the reaction, the dinitriles VIII, IX, X and XI containing carbonyl-, ester- and nitro groups were evaluated as to their polymerizability with formaldehyde. Under a variety of conditions, compound VIII reacted with formaldehyde to yield only small amounts of oils; this is indicative of the formation of a low molecular weight polymer. Analytical data were obtained for a sample which had been dried with great difficulty to a film in vacuo; the results were reasonable for a polymer having the unit structure $-HNCO(CH_2)_2C(CO-$

(10) D. T. Mowry and E. L. Ringwald, U. S. Patent 2,537,689 (1951).

(11) H. Feuer and S. M. Pier, This Journal, 74, 4706 (1952).

TABLE I

POLYAMIDES FROM FORMALDEHYDE[a] AND DINITRILES

Dinitrile	Reactn. medium	Reactn. time min.	Yield, %	M.p., °C.	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found	Product
$(NCCH_2CH_2)_2NCOCF_3$	A[b]	120	75	75–85	40.46	40.01	4.53	4.42	15.73	16.10	$(C_9H_{12}O_3N_3F_3)_n$
$(NCCH_2CH)_2NSO_2C_6H_5$	A	120	90	70–80	50.13	50.81	5.50	5.55	13.50	13.60	$(C_{13}H_{17}O_4N_3S)_n$
$(NCCH_2CH_2)_2NCOC_6H_5$	A	90	50	150–165	61.08	60.77	6.23	7.00	15.27	16.37	$(C_{14}H_{17}O_3N_3)_n$
$(NCCH_2CH_2)_2NCOC_6H_3(NO_2)_2$	A	120	80	165–185	46.02	45.87	4.14	4.24	19.17	19.45	$(C_{14}H_{15}O_7N_5)_n$
$(NCCH_2CH_2)_2C(CH_3)(COCH_3)$	A	120	20	220 (dec.)	58.38	56.50	8.02	7.56	12.38	11.59	$(C_{11}H_{18}O_3N_2)_n$
$(NCCH_2CH_2)_2C(CO_2C_2H_5)_2$	A	95	93	180–195	53.49	53.50	7.06	7.20	8.91	9.26	$(C_{14}H_{22}O_6N_2)_n$
$(NCCH_2CH_2)_2C(NO_2)_2$	B[c]	120	70	130–190	36.91	35.97	4.65	4.37	27.53	20.68	$(C_8H_{12}O_6N_4)_n$
$NC(CH_2)_2CN$	A	90	95	300 (dec.)	46.90	44.18	6.29	6.20	21.90	21.82	$(C_5H_8O_2N_2)$

[a] Trioxane was the source of formaldehyde. [b] A was prepared from 90% HCO_2H and 95% H_2SO_4. [c] B was prepared from 90% HCO_2H, 95% H_2SO_4 and CF_3CO_2H.

$CH_3)(CH_3)(CH_2)_2CONHCH_2–$. Some significance may be attached to the fact that ketones are basic (in the Lewis sense) in that they accept protons from strong acids. If the presence of the carbonyl group is in any way related to the difficulty in obtaining a high molecular weight polymer, it might be supposed that *two* carbonyl groups would produce an even more marked effect. For this reason, compound IX was treated with formaldehyde and all efforts to effect polymerization resulted in failure. The dinitrile was quite insoluble in the reaction medium, even when higher acid concentrations, higher temperatures, or more solvent were used. A significant fraction of the dinitrile was lost during these attempted polymerizations, and a blank experiment (no formaldehyde present) showed this phenomenon to be a result of the high temperatures and strongly acid conditions.

Upon reaction with formaldehyde, compounds X and XI gave the expected polyamides. Thus the carbethoxy groups in X survived the strongly acidic conditions of the reaction medium. A slight modification of the usual polymerization procedure was necessary with compound XI. The reaction as originally carried out in 90% formic acid and concd. sulfuric acid resulted in partial gelation, yielding gummy products which were difficult to purify. Upon addition of trifluoroacetic acid fluidity was maintained throughout the reaction. Despite the strong acidity ($K_{25} = 0.5$) of trifluoroacetic acid, polymerization did not occur until sulfuric acid was added.

The polyamides discussed above were soluble to varying degrees in acetone, dioxane, and dimethylformamide but insoluble in ethanol and water.

A polyamide was obtained from the reaction of succinonitrile and formaldehyde. It was high melting and insoluble in all the solvents tried. A polymer of similar characteristics has been described very recently.[12] The results of the elemental analysis, which were not in good agreement with the theory, might be attributed to contamination with methylenebissuccinimide formed in the reaction.[13] The infrared spectrum showed well defined absorption maxima at 3.06 and 6.08 μ which are characteristic of the peptide linkage.

(12) D. T. Mowry, U. S. Patent 2,617,786 (1952).
(13) This suggestion of one of the referees is gratefully acknowledged. Magat, *et al.*,[8] noted the formation of methylene-bis-phthalimide from o-phthalonitrile and formaldehyde.

The polyamides which appear in Table I were made by analogous procedures.

In the course of this work various improved methods of obtaining some of the starting materials have been developed.

Compound IX had been obtained in a 50% yield by the cyanoethylation of 2,4-pentanedione.[14] By using a slightly higher reaction temperature IX was secured in 73% yield.

Compound X had been synthesized by the cyanoethylation of ethyl malonate.[15] Several attempts to repeat the reaction failed and most of the acrylonitrile polymerized. This was probably due to the presence of peroxides in the dioxane solvent. When the reaction was carried out in dioxane which had been freed of peroxides, the product was obtained. However, *t*-butyl alcohol was found to be an even more satisfactory solvent, and no prior purification was required. The desired compound was obtained in a yield of 88%.

The preparation[16] of compound XI was improved to a one-step process which resulted in higher yields. Acrylonitrile reacted in the presence of potassium hydroxide with 2,2-dinitro-1,3-propanediol.[17] The diol was thereby demethylolated *in situ* to the salt of dinitromethane which then added to the acrylonitrile.

Experimental[18]

Polymerization of Succinonitrile and Formaldehyde.— The following procedure is representative of the preparation of the various polyamides. In carrying out the polymerization reaction, the *s*-trioxane was dissolved in formic acid *prior* to the addition of sulfuric acid. (If it was added to the mixture of the two acids, solution was attained with difficulty.) It was also found advantageous to cool the formic acid solution during the addition of sulfuric acid to avoid generation of carbon monoxide.

A solution of 0.6 g. of *s*-trioxane (0.02 mole of HCHO) and 3.7 ml. of concd. sulfuric acid in 10 ml. of 90% aqueous formic acid was warmed to 30–35°. At this temperature, 1.6 g. (0.02 mole) of succinonitrile was added in small portions, and stirring was carried on for 1.5 hours. When the clear solution was added to 200 ml. of water at 5°, a white solid precipitated. The solid was filtered off, washed thoroughly with water, reslurried in water, filtered and dried. A yield of 98% was obtained. When heated, the solid darkened above 220°, and decomposed at about 300°.

In the polymerization of 4,4-dinitroheptanedinitrile with formaldehyde the above procedure was slightly modified by

(14) G. R. Zeller and R. Levine, *J. Org. Chem.*, **13**, 911 (1948).
(15) H. A. Bruson and T. W. Riener, THIS JOURNAL, **65**, 23 (1943).
(16) L. Herzog, *et al.*, *ibid.*, **73**, 749 (1951).
(17) H. Feuer, *et al.*, *ibid.*, **73**, 1360 (1951).
(18) Unless otherwise indicated, melting points are uncorrected.

the addition of 5 ml. of trifluoroacetic acid to the reaction mixture.

4,4-Dinitroheptanedinitrile.—In a 500-ml. three-necked flask was placed 50 g. (0.3 mole) of 2,2-dinitro-1,3-propanediol, 320 ml. of water and 5 g. (0.09 mole) of potassium hydroxide. Over a period of 30 minutes, 90 ml. (1.35 moles) of acrylonitrile was added dropwise, while the temperature was kept at 30°. After the addition of acrylonitrile was complete, the solution was stirred for 6 hours, during which time it turned red. Enough 30% potassium hydroxide was added to bring the pH to 8, and then the solution was stirred for another 3 hours. The reaction mixture became heterogeneous, consisting of a red aqueous phase and a deep red, dense oil. Extraction of the aqueous phase with three 75-ml. portions of ether gave a solid when the ether had evaporated. Recrystallization of the solid from methanol yielded two crops of crystals, weighing 7.75 and 1.65 g., m.p. 78°. The heavy oil was triturated with 25 ml. of ether, and this treatment caused solidification. The solid was collected on a suction filter and freed of adhering oil. Recrystallization from methanol yielded two crops of crystals weighing 8.61 and 2.75 g., m.p. 77–78°.[16] The total weight of 20.76 g. represented a yield of 37%, based on 2,2-dinitro-1,3-propanediol.

N-Bis-(2-cyanoethyl)-trifluoroacetamide.—A round-bottomed flask was fitted with a reflux condenser, the top of which was connected to a trap surrounded by a Dry Ice–acetone-bath. Any vapors which passed through the condenser would thus liquefy in the cold trap. A solution of 50 g. of trifluoroacetic acid and 92 g. of benzoyl chloride was heated in the flask, and when the temperature reached 65°, gas was evolved. Over a period of 2 hours, the temperature was raised to 180°, and all substances boiling below 15° condensed in the cold trap. The product was mainly trifluoroacetyl chloride, mixed with some hydrogen chloride.

A solution of 100 g. of β,β'-iminodipropionitrile in 50 ml. of chloroform was rapidly stirred while the crude trifluoroacetyl chloride was distilled into it. A white solid immediately formed and the reaction was carried on for 5 hours. The solid was filtered off, and it was identified as the hydrochloride of β,β'-iminodipropionitrile[11]; 66 g. was obtained. After the chloroform had been removed from the filtrate, the residue was distilled through a 12″ Vigreux column, yielding a water-white liquid boiling at 158° at 0–1 mm., $n^{20}D$ 1.4398.

Anal. Calcd. for $C_8H_8OF_3N_3$: C, 43.83; H, 3.68; N, 19.14. Found: C, 43.97; H, 3.39; N, 19.40.

N-Bis-(2-cyanoethyl)-3,5-dinitrobenzamide.—A solution of 4.92 g. (0.04 mole) of β,β'-iminodipropionitrile in 20 ml. of chloroform was cooled and rapidly stirred. Upon the addition of 4.55 g. (0.02 mole) of 3,5-dinitrobenzoyl chloride dissolved in 30 ml. of chloroform, a white solid formed. Stirring was carried on for 2 hours, and then the solid was

removed by filtration. The total weight (dry) was 8.8 g.; the solid was a mixture of the desired product and the hydrochloride of β,β'-iminodipropionitrile. The product was extracted with water to remove the soluble hydrochloride, leaving behind 5.4 g. of a tan solid melting at 123–125°. Recrystallization from ethanol yielded short needles melting at 144–145°. When this solid was mixed with pure β,β'-iminodipropionitrile hydrochloride (m.p. 147–148°) melting occurred at 134–136° with the development of a green color. Thus, the desired N-bis-(2-cyanoethyl)-3,5-dinitrobenzamide melts close to β,β'-iminodipropionitrile hydrochloride.

Anal. Calcd. for $C_{13}H_{11}O_5N_5$: C, 49.22; H, 3.49; N, 22.08. Found: C, 49.90; H, 3.70; N, 21.64.

N-Bis-(2-cyanoethyl)-benzylamine.—A solution of 24.6 g. (0.2 mole) of β,β'-iminodipropionitrile and 12.7 g. (0.1 mole) benzyl chloride in 30 ml. of chloroform was stirred and heated to reflux for 12 hours. A solid slowly formed, and this was removed by suction filtration. As the chloroform solvent was removed, more solid formed, which was identified as the salt of β,β'-iminodipropionitrile, and this too was removed by filtration. The dense yellow residue was cooled to −75°, but no crystals appeared. Distillation through a short Vigreux column gave a very pale liquid boiling at 176° and 0.5 mm., $n^{20}D$ 1.5275. This was identified as N-bis-(2-cyanoethyl)-benzylamine.

Anal. Calcd. for $C_{12}H_{15}N_3$: C, 73.21; H, 7.09; N, 19.70. Found: C, 73.45; H, 7.14; N, 19.81.

Attempted Polymerization of N-Bis-(2-cyanoethyl)-benzylamine with Formaldehyde.—A solution of 0.195 g. of s-trioxane (6.5 mmoles of HCHO) and 1 ml. of concd. sulfuric acid in 5 ml. of 90% formic acid was warmed to 30–35°. During the addition of 1.36 g. (6.4 mmoles) of N-bis-(2-cyanoethyl)-benzylamine, the temperature rose and an ice-water bath was used to keep it at 30–35°. After stirring for 75 minutes, the clear solution was poured into 50 ml. of water at 5°, but no solid material formed. No solid was obtained when a sample of the solution was treated with sodium chloride. However, when the solution was basified with excess 20% aqueous sodium hydroxide, a milky emulsion formed. This mixture was extracted with ethylene chloride, which cleared up the emulsion. Removal of the ethylene chloride left behind 1.09 g. of a dense liquid which was identified as N-bis-(2-cyanoethyl)-benzylamine by its refractive index.

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[Contribution No. 195 from The Goodyear Research Laboratories]

The Synthesis and Polymerization of Some Allyl Esters of Carbamic Acid

By C. E. Gleim

A number of allyl esters of carbamic acid have been synthesized. Their properties, as well as those of some of their polymers, are reported.

A convenient method of synthesizing allyl carbamates is the reaction of allyl chloroformate with amino compounds. The reactions are generally carried out at a temperature of $0 \pm 10°$ in the presence of pyridine as an acid acceptor. A general procedure for their preparation is the dropwise addition of the chloroformate with stirring to a cold solution of the amino compound in pyridine. The resulting mixture is then poured into cold dilute hydrochloric acid from which the carbamate is separated, washed with dilute sodium bicarbonate solution, and purified.

The aldehyde condensation derivatives of the carbamates are prepared by treating an aldehyde with a carbamate in the presence of an acid catalyst. The general procedure for their preparation is the addition of an acid catalyst with cooling to a stirred solution of the aldehyde and carbamate followed by the addition of water, neutralization and purification.

Table I lists the allyl carbamates which have been prepared and indicates the source of each ester as well as the percentage yield. Certain physical properties of the esters are reported in Table II.