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CHEMISTRY OF DINITROACETONITRILE—II

DERIVATIVES OF DINITROACETONITRILE FROM MICHAEL, MANNICH AND ALKYLATION REACTIONS. 2,2-DINITRO-2-CYANOETHANOL AND ITS DERIVATIVES

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Abstract Addition of dinitroacetonitrile to carbonyl conjugated unsaturated systems was a generally successful reaction for the preparation of Michael adducts. The expected products were obtained with methyl acrylate, acrylamide, acrolein, butenone, methylene-bis-acrylamide, and N,N',N''-triacrylylperhydro-s-triazine. Acrylic acid gave three products: the normal adduct, the corresponding carbamyl derivative and its cyclic imide.

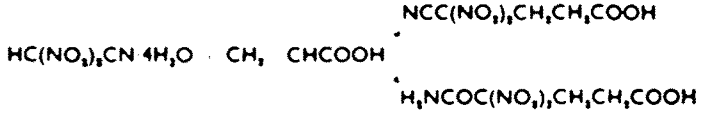
Dinitrocyanoethanol was easily prepared by reaction of dinitroacetonitrile with formaldehyde and the acetate, trifluoroacetate, acrylate and methacrylate esters of this alcohol were characterized. Esterification with 3,5-dinitrobenzoylchloride, fumaryl chloride and succinyl chloride gave liquid esters which could not be purified.

N-(2,2-Dinitro-2-cyanoethyl)amides could be prepared in relatively general fashion as the products of reaction of dinitroacetonitrile with N-methylolamides. The corresponding acetyl, benzoyl, acrylyl, methacrylyl and bis-urea derivatives are described. These compounds were sensitive toward hydrolysis.

Alkylation of dinitroacetonitrile and its salts to give identifiable products was not generally successful. As special cases the C-allyl, O-methyl, C-t-butyl and N-t-butyl derivatives could be prepared and were characterized.

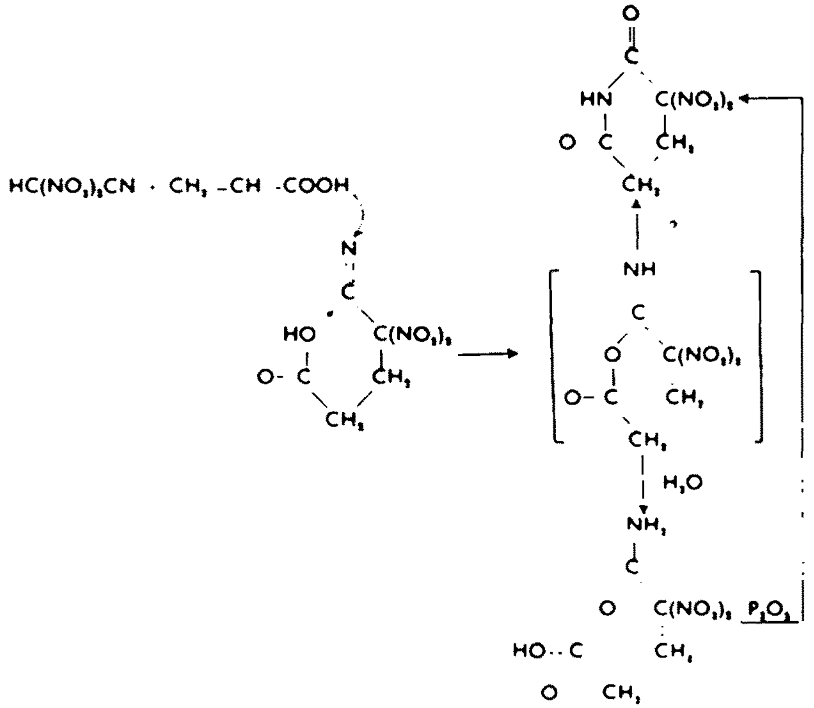
Derivatives of dinitroacetonitrile in which the dinitrocyanomethyl group was covalently linked via a carbon carbon bond were found to be obtained from three different types of reaction. Of these, addition of dinitroacetonitrile tetrahydrate to carbonyl-conjugated double-bond systems was the most generally successful product producing type of reaction studied. The resulting Michael adducts were obtained in good yields, were relatively easily purified and were no more susceptible toward hydrolysis and adventitious decomposition of the dinitrocyanomethyl group than were the carbon-substituted alkyl derivatives. The presence of β-carbonyl groups complicated the infrared spectra of these molecules and also their behavior in alkaline decomposition reactions but on both counts these complications were less troublesome than those encountered in dealing with other types of derivatives. The Michael adducts prepared have been listed in Table 1 together with data pertinent to the reactions and products.

A curious feature of dinitroacetonitrile chemistry which was encountered was the variety of products obtained from the Michael addition reaction of dinitroacetonitrile with acrylic acid. These were identified as the expected normal adduct, 4,4-dinitro-4-cyanobutyric acid, which was a minor rather than a principal product and 4,4-dinitro-4-carbamylbutyric acid, which was the principal product of the reaction in aqueous media and even when the addition was performed in t-butyl alcohol solution.[1] Formation of the carbamyl adduct cannot be attributed to secondary hydrolysis of the normal adduct through the agency of the water present in dinitroacetonitrile tetrahydrate because Michael addends other than acrylic acid showed no sort of corresponding behavior (see Table 1).



When acrylic acid was treated with anhydrous dinitroacetonitrile in ethyl acetate solution a product was obtained which was isomeric with the normal adduct and which was designated as α,α-dinitroglutarimide on the basis of its infrared absorption characteristics, elementary analysis and alternative preparation by treatment of the above carbamyl derivative with P_2O_5.

This diversity of related products obtained from the acrylic acid-dinitroacetonitrile reaction may be accounted for most readily by postulating cyclization of the normal adduct (4,4-dinitro-4-cyanobutyric acid) resulting from intramolecular nucleophilic attack of the carboxyl group on the electron deficient cyano-group, i.e. the site which was observed to be attacked by hydroxide ion in degradation experiments (see below):



The relationship between the postulated cyclic intermediate (bracketed structure) and the α,α-dinitroglutarimide structure remains unresolved. If it were not for the experimental observations that, firstly, the carbamyl-adduct was obtained copiously through the evident agency of relatively little water in the reaction mixture, and

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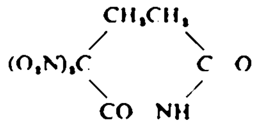
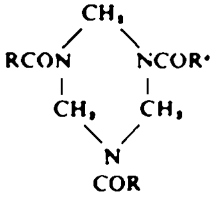
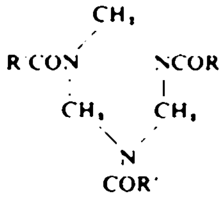
[1] Use of t-butyl alcohol avoided esterification of the carboxyl group

TABLE 1. MICHAEL REACTIONS OF DINITROACETONITRILE

Michael addend	Dinitroacetonitrile	Solvent	Reaction hr	Reaction temp	Product	m.p. b.p.	Product % yield
$CH_2{=}CHCOOMe$	tetrahydrate	methanol	5	60	$(O_2N)_2C(CN)CH_2CH_2COOMe$	78-80/0.12-0.15 mm	21
$CH_2{=}CHCONH_2$	anhydrous[a]	ether	24	36	$(O_2N)_2C(CN)CH_2CH_2CONH_2$	62-63	29
$CH_2{=}CHCOOH$	tetrahydrate	water	15	35	$(O_2N)_2C(CN)CH_2CH_2COOH$	73-74°	13
			16	25°	$(O_2N)_2C(CONH_2)CH_2CH_2COOH$	115-117°	60
$CH_2{=}CHCOOH$	tetrahydrate	t-butanol	14	40°	$(O_2N)_2C(CONH_2)CH_2CH_2COOH$	111-113°[b]	69
$CH_2{=}CHCOOH$	anhydrous[a]	ethyl acetate	12	40°		146-148	34
$CH_2{=}CHCHO$	tetrahydrate	water	40	25°	$(O_2N)_2C(CN)CH_2CH_2CH(OCH_3)_2$[c]	80-81/0.4 mm	57[d]
$(CH_2{=}CHCONH)_2CH_2$	tetrahydrate	water	7	55°	$[(O_2N)_2C(CN)CH_2CH_2CONH]_2CH_2$	133-134°	51
	tetrahydrate	methanol	15	40°		140-141°	26
$CH_2{=}CHCOCH_3$	tetrahydrate	water	120	25	$(NO_2)_2C(CN)CH_2CH_2COCH_3$	75/0.2 mm[g]	68

[a] Prepared *in situ* by neutralizing the sodium salt with sulfuric acid.
[b] No depression in mixed melting point with product of m.p. 115-117°.
[c] After subsequent reaction of crude product with methyl orthoformate.
[d] Yield of crude acetal.
[e] R = $(CH_2{=}CH_2-)$.
[f] R' = $[(O_2N)_2C(CN)CH_2CH_2-]$.
[g] In falling film still.

secondly, that the product designated as α,α-dinitroglutarimide was relatively unaffected by water (see Experimental) it would be tempting to conclude that the dehydro-product actually possessed the imino-anhydride structure. A more sophisticated structure elucidation was not feasible at the time this work was in progress.

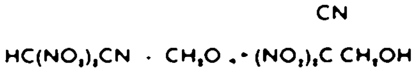
The Michael adduct obtained from methyl acrylate could be hydrolyzed quantitatively to succinic acid.

$$(NO_2)_2C(CN)CH_2CH_2COOCH_3 \xrightarrow[H_2O]{HCl} HOOCCH_2CH_2COOH$$

Although attempts to prepare a Michael adduct of dinitroacetonitrile with acrylonitrile were unsuccessful, this product was obtained by dehydration of 4,4-dinitro-4-cyanobutyramide in 30% yield.

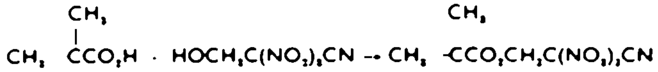
$$(NO_2)_2C(CN)CH_2CH_2CONH_2 \xrightarrow{P_2O_5} (NO_2)_2C(CN)CH_2CH_2CN$$

Reaction of dinitroacetonitrile with formaldehyde yielded 2,2-dinitro-2-cyanoethanol, a genuine carbon-alkylation product. This derivative was easily prepared but less easily purified since it tended to retain excess formaldehyde and to undergo retrogression.



$$HC(NO_2)_2CN + CH_2O \rightarrow (NO_2)_2\overset{CN}{C}CH_2OH$$

A number of esters of dinitrocyanoethanol were prepared. These included the trifluoroacetate, acetate, acrylate, and methacrylate. The acetate and methacrylate were obtained by reaction of the alcohol with the appropriate acid in the presence of trifluoroacetic anhydride as the condensing agent.



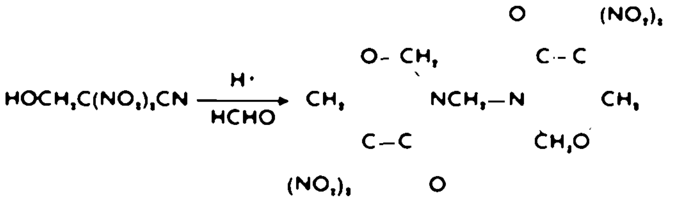
$$CH_2{=}\overset{CH_3}{C}CO_2H + HOCH_2C(NO_2)_2CN \rightarrow CH_2{=}\overset{CH_3}{C}CO_2CH_2C(NO_2)_2CN$$

All of the esters of dinitrocyanoethanol were noticeably fragile toward moisture catalyzed decomposition. Bulk polymerization of the methacrylate with azo-bis-isobutyronitrile as the catalyst gave a hard but somewhat discolored polymer. An attempt to prepare the methacrylate by azeotropic distillation of water from a mixture of 2,2-dinitro-2-cyanoethanol and anhydrous methacrylic acid in benzene gave a quantitative yield of water but a polymerized product. The mixed anhydride technique was also used to obtain 2,2-dinitro-2-cyanoethyl acrylate, but even careful fractionation failed to separate completely the acrylate from the trifluoroacetate formed in the esterification reaction. However, a pure sample of the acrylate was obtained in 49 per cent yield by esterification of 2,2-dinitro-2-cyanoethanol with acrylyl chloride in the presence of aluminum chloride; this procedure proved to be the more satisfactory one for the methacrylate. Bulk polymerization of both monomers with azo-bis-isobutyronitrile gave a gummy mass.

Esterification of 2,2-dinitro-2-cyanoethanol with fumaryl chloride, succinyl chloride and 3,3-dinitrobenzoyl chloride gave in each case a liquid product which on the basis of infrared examination appeared to be the desired ester. However, these liquids could not be crystallized even at Dry Ice temperatures and all decomposed on attempted distillation.

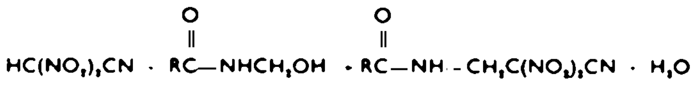
Nitration of 2,2-dinitro-2-cyanoethanol with a mixture of concentrated nitric and sulfuric acids gave a 67 per cent yield of a liquid which on the basis of its infrared spectrum appeared to be largely the desired nitrate ester. It was possible to distill this product and a fraction boiling at 46-55°/1 mm showed the expected nitrate absorption band at 1678 cm^{-1} and the dinitrocyanomethyl band at 1600 cm^{-1}. The nitrogen value obtained on elemental analysis was low, however, indicating the material was impure. The product appeared to be quite unstable since a sample became acidic fairly rapidly on standing. For this reason work with this compound was abandoned.

When an attempt was made to hydrolyze the nitrile group in 2,2-dinitro-2-cyanoethanol with concentrated sulfuric acid a product was isolated in fair yield which was believed to be a cyclic methylene-bis-amide. It was established that this product was formed by a reaction with the excess formaldehyde dissolved in the dinitrocyanoethanol, and the same product was obtained in much better yield when additional formaldehyde was used.



The analysis, infrared spectrum, and solubility properties of this product were in agreement with the proposed structure.

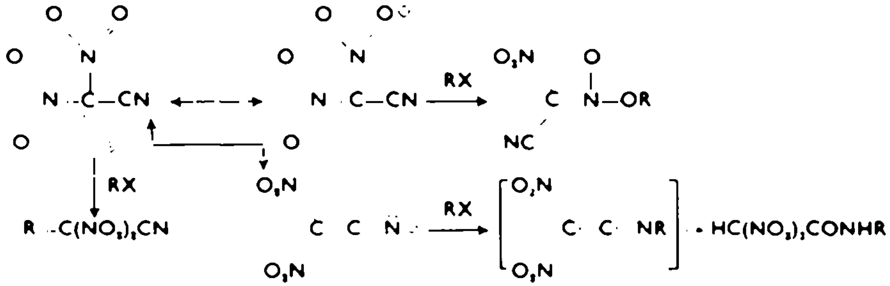
Several attempts were made to prepare Mannich-type derivatives through reaction of dinitrocyanoethanol with amides and ammonium salts. In several instances unelucidated interaction took place, but no dinitrocyanomethyl-derivatives could be prepared in this way. Under rather limited environmental conditions N-(2,2-dinitro-2-cyanoethyl) amides could be prepared through the reaction of dinitroacetonitrile with N-methylolamides.



$$HC(NO_2)_2CN + R\overset{\overset{O}{\|}}{C}-NHCH_2OH \rightarrow R\overset{\overset{O}{\|}}{C}-NH-CH_2C(NO_2)_2CN + H_2O$$

In most cases successful isolation of product seemed to depend upon choice of a relatively non-polar solvent medium, such as ethyl acetate, the presence of a drying agent to remove water formed in the reaction and judicious separation of excess reactants. Dinitrocyanoethylamides showed a much greater proclivity toward solvolysis than esters of dinitrocyanoethanol. In the presence of strong base however, a competitive type of direct attack on undissociated dinitrocyanoethylamide was observable. Thus when dinitrocyanoethylacetamide was dissolved in cold aqueous ethanol and was titrated immediately, neutral equivalent values as low as 137 were obtained. If complete preliminary hydrolysis were insured by warming the solution on the steam bath or allowing it to stand overnight before titration, values in good agreement with the theoretical neutral equivalent (202) were obtained.

Reactions of the dinitrocyanomethide ion with organic halides gave products which represented covalent bond formation derived from all three possible contributing structures of the ion:



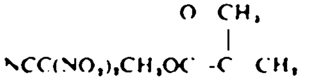
Of the organic halides which were investigated only methyl, allyl and t-butyl halides gave rise to stable, isolable products. Of these only allyl and t-butyl produced carbon-alkylated products. Since the same products which were isolated from alkylation of silver dinitrocyanomethide with t-butyl halide were also formed in reactions of t-butyl alcohol with dinitroacetonitrile tetrahydrate, it seems evident that these reactions were functions of the t-butyl carbonium ion. The structure of the products, then, reflected indiscriminate attack of the t-butyl carbonium ion on at least two of the three contributing structures of which the dinitrocyanomethide ion consists. A third, unidentified product was formed in these reactions which may or may not have been derived from an intermediate t-butyl nitronate. Fortunately the mixture of carbon and nitrogen t-butyl alkylated products was easily separated by making use of the difference in their chemical properties. The carbon alkylated product, 2,2-dinitro-3,3-dimethylbutyronitrile, was most easily soluble in non-polar solvents and unaffected by mild exposure to aqueous acids and bases. The nitrogen alkylated product emerged from reaction mixtures as N-t-butyl-α-α-dinitroacetamide, easily soluble in dilute aqueous alkali and insoluble enough in water to be precipitated by acidification.

Methyl iodide reacted with silver dinitrocyanomethide in most solvent systems. The best yields of stable, isolable product were obtained from heterogeneous mixtures containing silver salt suspended in excess methyl iodide. Identification of this product as the oxygen alkylated derivative was finally made on the basis of its ultraviolet absorption spectrum, which showed a strong maximum near 300 mμ, and from study of its hydrolysis products from acidic and basic solutions. The nitronate structure gave absorption bands in the 6 μ region of its infrared spectrum which could be ambiguously interpreted. However, the above-mentioned bona fide carbon alkylated derivatives were sharply distinguished by the absence of long wave length ultraviolet absorption. The nitronate structure was further corroborated by solvolytic fragmentation into dinitrocyanomethide ions and formaldehyde.

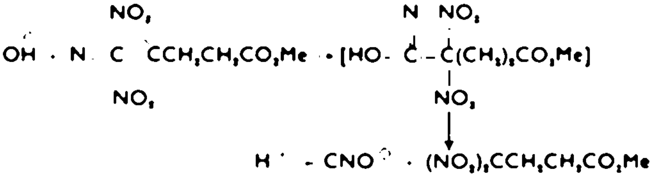
It was observed quite early in the work with organic derivatives of dinitroacetonitrile that most of these compounds had reproducible neutral equivalents and could be titrated with base. Generally two equivalents of base were consumed per mole of dinitrocyanomethyl groups and in most cases the titration could be carried out with sodium hydroxide to a phenolphthalein end point (Table 2).

The behavior of methyl 4,4-dinitro-4-cyanobutyrate with base was studied in some detail. The ester reacted rapidly with methanolic potassium hydroxide, potassium cyanide, or sodium methoxide to give in each case quantitative yields of a yellow solid which was recrystallizable from hot methanol. This material proved to be the potassium salt of methyl 4,4-dinitrobutyrate. Repeated recrystallization of the salt resulted in an analytically pure sample which was converted to the distillable dinitro compound,

TABLE 2. NEUTRAL EQUIVALENTS OF DINITROCYANOMETHYL DERIVATIVES

Compound	MW	Neut equiv	Equivalents used per mole
$NCC(NO_2)_2(CH_2)_2COOH$	203	68·6	3
$NCC(NO_2)_2(CH_2)_2COOCH_3$	217	105·8	2
$NCC(NO_2)_2(CH_2)_2CONH_2$	202	105·0	2
 $NCC(NO_2)_2CH_2O\overset{O}{C}-\overset{CH_3}{C}{=}CH_2$	229	113·5	2

methyl 4,4-dinitrobutyrate. This material was characterized by reaction with methyl acrylate to give dimethyl 4,4-dinitropimelate, m.p. 46°. The inorganic residue from the alkaline degradation was examined and found to contain mostly potassium cyanate. Thus the overall reaction appears to involve nucleophilic attack on the nitrile group.



EXPERIMENTAL

Alkylation Products of Dinitroacetonitrile 4,4-Dinitro-4-Cyanobutene-1

To a solution of 28·7 g (0·12 mole) of silver dinitrocyanomethide in 300 ml of acetonitrile was added 18·0 g (0·148 mole) of allyl bromide. After heating at 40–45° for 3 hr, 9·2 g of silver bromide was isolated. An additional 2 g of allyl bromide was added to the reaction mixture and after heating for 4 hr at 40–60° another 7·6 g of silver bromide was obtained. Five grams of allyl bromide was added, and the solution was allowed to stand for two days. Altogether 21·1 g (94%) of silver bromide was collected. Most of the solvent was removed under reduced pressure. The residue was dissolved in ether, washed with water, with 5% sodium bicarbonate solution, with water again, and was then dried with anhydrous magnesium sulfate. After removal of solvent there remained 10·4 g of residue. This was flash distilled from a bath at 85–90° at 0·5–1·5 mm to yield 7·1 g (35%) of crude 2,2-dinitro-4-pentenenitrile, n_D^{20} 1·4558. This material was fractionally distilled through a Holtzman Column. A 3·5 g portion which distilled at 38–40°/0·4 mm was analyzed and its infrared spectrum measured, n_D^{20} 1·4552.

(Found: C, 34·63; H, 2·67; N, 23·77. Calc for $C_5H_5O_4N_3$: C, 35·08; H, 2·92; N, 24·56.)

"Methyl Dinitroacetonitrile," Dinitroacetonitrile-O-Methylether

To 250 g (1·76 moles) of stirred methyl iodide was added 41·8 g (0·176 mole) of silver dinitrocyanomethide over a 15 min period. The resulting mixture was stirred at room temperature for 1 hr and then diluted with an equal volume of ether. The solution was allowed to stand 1 hr and 39 g (94%) of silver iodide was collected on a funnel and washed with water to remove any unreacted silver dinitrocyanomethide. The ethereal filtrate was evaporated under reduced pressure to yield

14.9 g (58.3%) of yellow solid, m.p. 57-60°. This material was sufficiently pure for most purposes. A small portion of the product was recrystallized from water to yield a cream colored solid, m.p. 62-64°. (Found: C, 24.51; H, 1.86; N, 28.70. Calc. for $C_3H_3N_3O_4$: C, 24.83; H, 2.08; N, 28.96.)

Solvolysis and Alkaline Decomposition of "Methyl Dinitroacetonitrile"

Samples of "methyl dinitroacetonitrile" were suspended in water which was heated to 50° and stirred while standard hydroxide solution was added continuously from a burette so as to maintain the pH of the solutions within the ranges indicated below. pH was determined with a Beckmann pH meter. The concentration of nitrite ion in the final solution was determined colorimetrically with Shinn reagent.[8] The concentration of dinitrocyanomethide ion was determined by measuring the extinction coefficient of the characteristic ultraviolet absorption band at 345 mμ. Formaldehyde was determined gravimetrically with methone. In experiments 6 and 7, the "methyl dinitroacetonitrile" was added to a 2.8-fold excess of potassium hydroxide dissolved in a mixture of equal volumes of ethylene glycol and isopropyl alcohol. After standing for 20 hr at 0° and 25°, respectively, the excess base was back-titrated. Nitrite ion was determined colorimetrically as above. Both solutions were examined for ultraviolet absorption at 345 mμ and from the absence of appreciable absorption it was concluded that dinitrocyanomethyl ion was not formed under these conditions.

TABLE 3. ALKALINE DEGRADATION OF "METHYL DINITROACETONITRILE"

Exp. no.	pH	Millimoles Sample	 Base	 Nitrite	 Dinitrocyano-methyl ion	 HCHO	Absorption max (mμ)
1	6.5-7.0	2.496	1.96[a]	0.58	1.667	not measured	345
2	8-9	2.28	2.40[a]	0.383	[b]	0.189	335
3	8-9	2.07	3.52	1.32	0.617	0.617	345
4	6-7	1.38	1.36	0.440	0.820	0.130	345
5	6-7	1.38[c]	3.20	0.348	[b]	0.142	335-345
6	—	1.05	0.93	0.80	0.0	not measured	—
7		1.03	1.08	0.50	0.0	not measured	

[a] Experiment terminated after 2-3 hr and complete reaction not assured.

[b] Concentration of dinitrocyanomethyl ion was made uncertain by extraneous absorption; the wavelength of ϵ_{max} was shifted.

[c] Methone (2.90 mmoles) added at beginning of the experiment.

Reaction of "Methyl Dinitroacetonitrile" with 2,4-Dinitrophenylhydrazine

A 2,4-dinitrophenylhydrazine reagent solution containing 2.7 g (0.014 mole) in a mixture of 70 ml of ethanol, 21 ml of water and 14 ml of sulfuric acid was prepared. "Methyl dinitroacetonitrile" (2.0 g, 0.014 mole) was added to this solution while it was stirred at room temperature. Complete dissolution took place as the temperature of the solution was raised to 50-55°, and maintained for thirty minutes. The solution was allowed to cool and stand for approximately sixty hours at room temperature. After cooling in an ice bath the mixture was filtered, giving 1.0 g (35% yield) of orange crystals, m.p. 158-159°. One recrystallization from ethanol raised the melting point to 161-162°. A mixture with authentic formaldehyde 2,4-dinitrophenylhydrazone (m.p. 162.5°-163.5°) melted at 161-163.5°.

Alkylation of dinitroacetonitrile with t-butyl alcohol. 2,2-dinitro-3,3-dimethylbutyronitrile and N-t-butyldinitroacetamide

The alkylation of dinitroacetonitrile with t-butyl alcohol to give 2,2-dinitro-3,3-dimethylbutyronitrile and N-t-butyl dinitroacetonitrile has been carried out under a variety of conditions. Dinitroacetonitrile both as the tetrahydrate and in the anhydrous form in solution was used. In some cases acetic acid and sulfuric acid were also introduced into the reaction media but their presence did not

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[8] M. B. Shinn, *Industr. Engng Chem. (Anal.)* 13, 33 (1941).

seem to be necessary. In an experiment where the reactants were dinitroacetonitrile in ether solution (prepared by acidification of the sodium salt with sulfuric acid), an additional mole of sulfuric acid and an excess of 2½ moles of t-butyl alcohol, a third, neutral, unidentified reaction product was also isolated. All three products were not isolated each time and the best yields of each were not obtained from any one experiment. As far as is known, all three products may be formed in every case, however.

A solution of 16.4 g (0.08 mole) of dinitroacetonitrile tetrahydrate and 12.4 g (0.08 mole) of sodium dinitrocyanomethide in 39.3 g (50 ml, 0.56 mole) of t-butyl alcohol was heated to 60° and stirred for 20 hr. A separate layer, presumably water saturated with sodium dinitrocyanomethide formed after 1 hr. The mixture was cooled, ether was added, and the lower layer was extracted with ether. Combined liquors and extracts were dried with magnesium sulfate before evaporating the solvent and excess t-butyl alcohol under reduced pressure. 2,2-Dinitro-3,3-dimethylbutyronitrile has a high vapor pressure and was speedily lost when evacuation was continued after solvent has been removed. The oily residue was extracted with petroleum ether which dissolved most of the 2,2-dinitro-3,3-dimethylbutyronitrile. Most of the N-t-butyldinitroacetamide remained in the oily residue. This residue was dissolved in ether and extracted with 5% sodium bicarbonate solution. Acidification of the bicarbonate extract with cold hydrochloric acid precipitated 1.2 g of solid material, m.p. 99–100°. The petroleum ether extract (above) was extracted with 5% sodium bicarbonate solution, and acidification of this bicarbonate extract gave another 0.3 g of solid material, m.p. 102–103°. These fractions were combined (1.5 g, 9.1%) and recrystallized from aqueous methanol several times; this raised the melting point to 110.5–111° (dec.).

(Found: C, 35.48; H, 4.70; N, 18.69; neut. equiv., 206.7. Calc. for $C_6H_{11}O_5N_3$(N-t-butyldinitroacetamide): C, 35.11; H, 5.40; N, 20.48; neut. equiv., 205.)

The petroleum ether extract (above) was concentrated at a low temperature. The concentrate when cooled to −70° gave white crystals which were recrystallized from aqueous ethanol, yield 2.1 g (13.6%) of product, m.p. 120° (dec). Successive recrystallizations from ethanol raised the melting point to 132–133° (dec.).

(Found: C, 38.75; H, 4.62; N, 21.84. Calc. for $C_6H_9O_4N_3$ (2,2-dinitro-3,3-dimethylbutyronitrile): C, 38.51; H, 4.85; N, 22.46.)

Isolation of the third product was carried out as follows: a suspension of 15.3 g (0.1 mole) of sodium dinitrocyanomethide in ether was treated with 10.2 g (0.1 mole) of sulfuric acid dropwise. After the sodium bisulfate was removed by filtration, the filtrate was added to 200 g (2.7 mole) of t-butyl alcohol, and 15 g (0.148 mole) of sulfuric acid was added to this solution. This mixture was kept at 50° for 24 hr. Removal of volatile material under reduced pressure left a heavy liquid which was extracted with two volumes of water to remove sulfuric acid and residual t-butyl alcohol, and was then dissolved in ether, washed twice with one-half volume of water and dried with magnesium sulfate. Evaporation of solvent left a solid residue which was washed onto a filter with 25% aqueous methanol. Yield of the residue was 11.0 g. This material was dissolved in warm benzene and N-t-butyl dinitroacetamide was precipitated by addition of petroleum ether. The filtrate was evaporated leaving a semi-solid residue. Addition of petroleum ether dissolved away 2,2-dinitro-3,3-dimethylbutyronitrile and left a solid, m.p. 162–165°, yield 1.3 g. Successive recrystallizations from aqueous methanol raised the melting point to 164–165°.

(Found: C, 50.90; H, 6.82; N, 25.43, mol. wt. (ebull., acetone), 268.)

Alkylation of Silver Dinitrocyanomethide with t-Butyl Bromide

To 55.0 g (0.40 mole) of t-butyl bromide immersed in a cooling bath was added with stirring 9.6 g (0.04 mole) of silver dinitrocyanomethide. The resulting mixture was stirred at room temperature for 2 hr and then diluted with 200 ml of ether. After standing overnight, 7.3 g (97%) of silver bromide was collected on a funnel and then washed with acetone to remove any unreacted silver dinitrocyanomethide. The ethereal filtrate was evaporated under reduced pressure to yield 9.1 g of a yellow oil, a mixture of 2,2-dinitro-3,3-dimethylbutyronitrile and N-t-butyldinitroacetamide. Separation of the mixture of nitrogen and carbon alkylated products was affected by dissolving the crude material in 250 ml portions of 5% sodium hydroxide. Evaporation of the ether under reduced pressure gave an oil, the absorption spectrum of which was identical to that of the previously prepared 2,2-dinitro-3,3-dimethylbutyronitrile. Sublimation of the oil at 60–70°/20 mm gave 1.3 g (17%) of a white, waxy solid (m.p. 120–124°) having a strong camphor-like odor. Infrared examination showed a dinitrocyanomethyl absorption band at 1595 cm⁻¹. The sample volatilized before elemental analyses were obtained. Acidification of the basic extract with dilute sulfuric acid liberated the amide which was crystallized from warm aqueous methanol to give 1·5 g (18%) of N-t-butyldinitroacetamide, m.p. 110–111° dec.

(Found: C, 35·42; H, 5·32; N, 20·93; neut. equiv. 204·0. Calc. for $C_6H_{11}O_5N_3$: C, 35·12; H, 5·41; N, 20·48; neut. equiv., 205·2.)

Methyl 4,4-Dinitro-4-Cyanobutyrate

A mixture of 24·0 g (0·128 mole) of dinitroacetonitrile tetrahydrate and 17·2 g (0·2 mole) of methyl acrylate in 35 ml of methanol was heated at 50° for 5 hr. During this period the solution became very dark. After standing overnight, volatile material was removed under reduced pressure. The liquid residue was dissolved in ether, washed with 5% bicarbonate solution and with water, and then dried over anhydrous magnesium sulfate. When the solvent was removed there remained 8·4 g of crude liquid. This material was flash distilled from a bath at 100–120°/0·05 mm yielding 5·8 g (21%) of pale yellow distillate. The infrared spectrum of this material showed a carbonyl ester band at 1739 cm⁻¹, the dinitrocyanomethyl band at 1600 cm⁻¹, and a weak cyano band at 2250 cm⁻¹. A portion of the product was redistilled. The entire sample came over at 78–80°/0·12–0·15 mm, n_D^{25} 1·4595.

(Found: C, 33·40; H, 2·28; N, 19·55. Calc. for $C_6H_7O_6N_3$: C, 33·18; H, 3·23; N, 19·35.)

Acid Hydrolysis of Methyl 4,4-Dinitro-4-Cyanobutyrate to Succinic Acid

A mixture of 1·2 g (0·0055 mole) of methyl 4,4-dinitro-4-cyanobutyrate and 15 ml of 20% hydrochloric acid was heated under reflux for 3 hr. When the mixture was cooled, a brown solid crystallized, yield 0·5 g (91%). Treatment with carbon during recrystallization from water yielded white crystals, m.p. 186–189°, neut. equiv. 60·5 (succinic acid, m.p. 188°, neut. equiv. 59). The infrared spectrum of this material showed it to be a dicarboxylic acid without any absorption bands attributable to ester, nitro, or nitrile groups.

4,4-Dinitro-4-Cyanobutyramide

A suspension of 12·5 g (0·08 mole) of sodium dinitrocyanomethide in 250 ml of ether was acidified by the dropwise addition of 4·2 g (0·041 mole) of sulfuric acid at room temperature. This suspension was stirred for 30 min and was then filtered to remove sodium sulfate. Recrystallized acrylamide, 5·8 g (0·08 mole) was dissolved in the ether filtrate with the addition of a little ethyl acetate to facilitate solution. The solution then was heated under reflux for 24 hr. About 0·5 g of insoluble material was removed by filtration. Solvent was evaporated from the filtrate leaving 12 g of partially crystalline residue. After addition of methylene chloride, 7·0 g of crystalline product was obtained. This was dissolved in ethanol and filtered to remove insoluble material. Benzene was added to the alcohol solution which was concentrated, yielding 5·9 g (29·0%) of crystalline material, m.p. 43–5°. After three recrystallizations from a chloroform–ethanol mixture, the product melted at 62–63°.

(Found: C, 29·96; H, 2·53; N, 27·58. Calc. for $C_5H_6O_5N_4$: C, 29·71; H, 2·99; N, 27·72.)

4,4-Dinitro-4-Carbamylbutyric Acid and 4,4-Dinitro-4-Cyanobutyric Acid

A solution of 14·5 g (0·204 mole) of glacial acrylic acid and 28·5 g (0·14 mole) of dinitroacetonitrile tetrahydrate in 15 ml of water was allowed to stand 48 hr at 25–35°. When volatile material had been evaporated under reduced pressure, there remained 29·6 g of crystalline solid, m.p. 95–112°. Recrystallization from a mixture of equal parts by volume of chloroform and benzene yielded 18·5 g (60%) of 4,4-dinitro-4-carbamylbutyric acid, m.p. 104–109°. After one recrystallization from an ether-chloroform mixture in the presence of the decolorizing carbon, three additional recrystallizations from the same solvent gave a colorless product which melted at 115–117°.

(Found: C, 27·45; H, 3·08; N, 19·24; neut. equiv., 74·8. Calc. for $C_5H_7O_7N_3$: C, 27·16; H, 3·17; N, 19·00; neut. equiv., 73·7.)

The filtrate from the first crystallization (chloroform–benzene solution) was evaporated, and after a second small crop of the above material was removed, the residue consisted of 3·7 g (13%) of 4,4-dinitro-4-cyanobutyric acid, m.p. 72–74°. After several recrystallizations from chloroform the product melted at 73–74°.

(Found: C, 29·34; H, 2·34; N, 20·39; neut. equiv., 68·6. Calc. for $C_5H_5O_6N_3$: C, 29·57; H, 2·48; N, 20·69; neut. equiv., 67·7.)

4,4-Dinitro-4-Carbamylbutyric Acid

To a solution of 4·0 g (0·056 mole) of acrylic acid in 11 ml of t-butyl alcohol was added 8·0 g (0·039 mole) of dinitroacetonitrile tetrahydrate. After the solution had been allowed to stand for 14 hr, solvent was evaporated under reduced pressure. The residue was triturated with chloroform and filtered, yielding 6·0 g (69%) of solid, m.p. 111–113°. No depression in melting point was observed during a mixed melting point with material prepared above (m.p. 115–117°). There appeared to be some of the normal (cyano-) adduct present in the chloroform filtrate, but this could not be purified readily.

α,α-Dinitroglutarimide

A solution of 10·0 g (0·065 mole) of sodium dinitrocyanomethide in 80 ml of ethyl acetate was acidified by the dropwise addition of 3·3 g (0·033 mole) of sulfuric acid at room temperature. After stirring for 30 min the mixture was filtered and 5·0 g (0·07 mole) of glacial acrylic acid was added to the filtrate. The reaction was allowed to proceed for 12 hr at 40°. Solvent was removed under reduced pressure leaving 15 g of residue. Extraction of the residue with ether and chloroform yielded 4·5 g (34%) of α,α-dinitro-glutarimide, m.p. 141–143°. Recrystallization, once from water and twice from an ethyl acetate–cyclohexane mixture, yielded α,α-dinitro-glutarimide which melted at 146–148°. The product was slightly acid. Its infrared spectrum did not have a nitrile absorption band and made the presence of a carboxyl group doubtful. The absorption band at 1578 cm^{-1} suggested the possibility of a dinitrocyanomethyl group. The infrared spectrum showed NH bands at 3160 and 3060 cm^{-1}; the presence of the second band is presumably due to the presence of some impurity, possibly the uncyclized product.

(Found: C, 30·07; H, 2·54; N, 20·96. Calc for $C_5H_5O_6N_3$: C, 29·57; H, 2·48; N, 20·69.)

Dehydration 4,4-Dinitro-4-Carbamylbutyric Acid to α,α-Dinitroglutarimide

A solution of 0·7 g (0·0032 mole) of 4,4-dinitro-4-carbamylbutyric acid, m.p. 115–117° in 30 ml of acetonitrile was treated with an excess of phosphorus pentoxide, and an exothermic reaction was observed. The mixture was stirred for 2 hr and then evaporated to dryness. The residue was extracted with ether. The ether extracts were evaporated leaving 0·3 g (46%) of material which melted at 148–150°. After recrystallization from a mixture of ethyl acetate and chloroform, the product melted at 150–151°. A mixture melting point with a sample prepared by the Michael addition reaction in t-butyl alcohol solution gave no depression, and the infrared spectra of both products were identical.

4,4-Dinitro-4-Cyanobutyraldehyde Dimethylacetal

Dinitroacetonitrile tetrahydrate, 9·2 g (0·045 mole), was added to a solution of 2·8 g (0·05 mole) of acrolein in 10 ml of water. After the solution had been allowed to stand for 40 hr, the amount of oil which had formed a lower layer was 8·0 g (96%). The oily layer was separated, dissolved in 30 ml of methanol, treated with 9·4 g (0·089 mole) of methyl orthoformate and 0·08 g of p-toluenesulfonic acid monohydrate and heated under reflux for 5 hr. All volatile material was removed under reduced pressure, leaving 6·6 g (66%) of yellow liquid which was distilled. The fraction which distilled at 80–81°/0·4 mm weighed 5·7 g (57%).

(Found: C, 35·83; H, 4·51; N, 18·68. Calc for $C_7H_{11}O_6N_3$: C, 36·05; H, 4·75; N, 18·01.)

The crude adduct from another reaction was flash distilled instead of converting it to the acetal. Material which distilled at 90–100°/1·0–0·55 mm amounted to 3·6 g (31%). During redistillation at 80–92°/0·75–1·3 mm, partial decomposition could not be avoided, and the product which was obtained was not of satisfactory purity.

(Found: C, 36·13; H, 2·80; N, 19·34. Calc for $C_5H_5O_5N_3$: C, 32·11; H, 2·69; N, 22·46.)

1,3,5-Tris-(γ,γ-Dinitro-γ-Cyanobutyryl)Perhydro-s-Triazine

Dinitroacetonitrile tetrahydrate, 9·0 g (0·044 mole) was added to a solution of 4·0 g (0·016 mole) of recrystallized 1,3,5-tri-acrylylperhydro-s-triazine in 250 ml of methanol, and the solution was stirred at 35–40° for 15 hr. Solvent was evaporated under reduced pressure leaving a mixture of oil and crystals. When this material was dissolved in ethanol, addition of chloroform caused crystallization of 2·5 g (26%) of product, m.p. 143–145°. This was recrystallized again from ethanol–chloroform without changing the melting point.

(Found: C, 34·14; H, 3·03; N, 26·09. Calc for $C_{18}H_{18}O_{15}N_{12}$: C, 33·66; H, 2·82; N, 26·17.)

Methylene-Bis-4,4-Dinitro-4-Cyanobutyramide

Dinitroacetonitrile tetrahydrate, 25·0 g (0·123 mole), was added to a solution of 10·0 g (0·065 mole) of recrystallized methylene-bis-acrylamide in 300 ml of water and the solution was stirred at 55° for 7 hr Most of the solvent was removed under reduced pressure The residue was dissolved in a little alcohol and crystallized after the addition of water to yield 8·0 g (31%) of product, m.p 134–135 After several recrystallizations from aqueous ethanol, the melting point was unchanged.

(Found C, 32·15; H, 2·62, N, 27·80 Calc for $C_{11}H_{12}O_{10}N_6$: C, 31·73; H, 2·91, N, 26·92)

5,5-*Dinitro*-5-*Cyanopentanone*-2

Addition of 5·0 g (0·07 mole) of methylvinyl ketone to a solution of 12·0 g (0·059 mole) of dinitroacetonitrile tetrahydrate in 15 ml of water was accompanied by slight evolution of heat Separation of the solution into two layers took place within a few minutes After the reaction mixture had been allowed to stand at room temperature for five days (this time was probably longer than necessary), the layers were separated The oily layer weighed 11·0 g, 92·5% crude yield It was washed three times with 35 ml portions of water, dissolved in ether and dried with magnesium sulfate After removal of drying agent and solvent, the residue was flash distilled from a bath at 100–104°/0·5–1·0 mm, giving 8·1 g (68% yield) of distillate, n_D^{20} 1·4650 Redistillation in conventional apparatus proved unsatisfactory because a steady pressure could not be maintained The product was redistilled through a falling-film still at 77°/0·2–0·5 mm giving a distillate with n_D^{20} 1·4646.

(Found: C, 36·62, H, 3·22; N, 20·53 Calc for $C_6H_7O_5N_3$: C, 35·82, H, 3·51, N, 20·89)

From the distillate a semicarbazone derivative was prepared by standard procedures After several recrystallizations from aqueous ethanol, the derivative melted at 137–138° (dec.).

(Found: C, 32·67, H, 3·86; N, 32·43 Calc for $C_7H_{10}O_5N_6$. C, 32·56; H, 3·88; N, 32·56)

The infrared spectrum of the ketone contained absorption bands attributed to the following functional groups nitrile at 2245 cm^{-1}, ketone carbonyl at 1721 cm^{-1} and dinitrocyanomethyl at 1599 and 1297 cm^{-1}

Mannich Type Reaction Products of Dinitroacetonitrile

These compounds have all been prepared successfully by the same general procedure, which is the best procedure developed thus far but does not represent the result of an intensive search for optimum conditions In every case dinitroacetonitrile was used as obtained by neutralizing sodium dinitrocyanomethide in ethyl acetate solution with one equivalent of sulfuric acid After stirring the mixture for 30 min, the sodium sulfate was removed by filtration and the filtrate was used as indicated

N-(2,2-*Dinitro*-2-*Cyanoethyl*)*Benzamide*

A solution of 5·0 g (0·033 mole) of N-methylolbenzamide[3] in 30 ml of ethyl acetate was stirred and heated to 50°. A solution of dinitroacetonitrile (0·033 mole) in 50 ml of ethyl acetate was added to it dropwise over a period of 2 hr The reaction mixture was maintained at a temperature of 50° for an additional 30 min and cooled All volatile material was removed by evaporation under reduced pressure. The viscous residue was extracted with methylene chloride and filtered to remove methylene-bis-benzamide When the solvent was again evaporated, the residue crystallized It was washed onto a filter with cold water containing a little ethanol and dried The weight of crude product amounted to 1·7 g (20%), m p 117–118° After recrystallization once from carbon tetrachloride and twice from benzene, the melting point increased to 119·5–120·5°.

(Found: C, 46·15, H, 2·40; N, 22·82 Calc for $C_{10}H_8O_5N_4$: C, 45·46, H, 3·03, N, 21·21)

N-(2,2-*Dinitro*-2-*Cyanoethyl*)*Acetamide*

A solution of 8·1 g (0·09 mole) of N-methylolacetamide[4] in 30 ml of ethyl acetate was stirred at room temperature and treated with a solution of dinitroacetonitrile (0·09 mole) in 50 ml of ethyl acetate About 5 g of anhydrous magnesium sulfate was added to the solution which was warmed to 30° and allowed to stand for 2 hr The solution was filtered and all volatile material evaporated from the filtrate under reduced pressure The viscous residue was shaken once with two to three volumes of ice water which was immediately decanted The residue was dissolved in ether and dried with magnesium sulfate After the mixture had been filtered again and solvent evaporated from the filtrate, the

[3] A Einhorn, *Liebigs Ann* 343, 207 (1905)

[4] A Chwala, *Chem Abstr* 43, 569 (1949)

residue crystallized when it was chilled. The weight of product was 5·5 g (33%), m.p. 70–73°. It was recrystallized from benzene to a constant melting point of 76·5–77·5°.

(Found: C, 29·47; H, 3·10; N, 27·51. Calc. for $C_5H_6O_5N_4$: C, 29·70; H, 2·97; N, 27·72.)

N-(2,2-*Dinitro-2-Cyanoethyl*) *Methacrylamide*

A mixture of 4·25 g (0·05 mole) of methacrylamide and 1·5 g (0·05 mole) of paraformaldehyde was ground together in a mortar. Two drops of nearly saturated aqueous potassium carbonate solution was added to the mixture and grinding was continued for 2–3 min. The mixture was scraped into a test tube and heated to 50–60° with stirring; it gradually melted to give a clear liquid. This was cooled, dissolved in 40 ml of dioxane and filtered. The solution was stirred while 14 g of pulverized Drierite was added to it. The suspension was heated to 40–45° and stirred while a solution of dinitroacetonitrile (0·05 mole) in 50 ml of ethyl acetate was added dropwise during a period of 2 hr. Heating at 40–45° was continued for 30 min. The mixture was cooled, filtered, and all volatile material evaporated from the filtrate under reduced pressure. The viscous residue was covered with one to two volumes of ice water, a few drops of ethanol were added and the mixture was triturated. The solid product, when filtered and dried, weighed 3·3 g (27%), m.p. 70–73°. After two recrystallizations from benzene the product melted at 74–75°.

(Found: C, 36·54; H, 2·78; N, 24·15. Calc. for $C_7H_8O_5N_4$: C, 36·84; H, 3·51; N, 24·56.)

N-(2,2-*Dinitro-2-Cyanoethyl*)*Acrylamide*

This preparation was carried out in exactly the same manner as the preceding one, using the same molar quantities of the analogous reagents. When all volatile material had been removed from the reaction mixture and the viscous residue was triturated with ice-water and a little ethanol, crystallization did not take place. The oily product was dissolved in ether, dried with magnesium sulfate, and the ether evaporated again. Addition of carbon tetrachloride and a little ether brought about crystallization after trituration in an ice-bath. The dried product weighed 2·1 g (20%), m.p. 80–82°. After two recrystallizations from benzene the melting point was 77–78°.

(Found: C, 34·14; H, 2·79; N, 26·44. Calc. for $C_6H_6O_5N_4$: C, 33·64; H, 2·80; N, 25·17.)

N,N′-*Bis-*(2,2-*Dinitro-2-Cyanoethyl*)*Urea*

Dimethylolurea, 13·2 g (0·11 mole) and anhydrous magnesium sulfate, 9·0 g (0·075 mole), were suspended in 100 ml of ethyl acetate and stirred at 12° for 5 hr while a solution of dinitroacetonitrile (0·22 mole) in ethyl acetate was added dropwise. Stirring at 12° was continued overnight and for 5 hr at room temperature the following day. Suspended solids were filtered and the volatile material was evaporated from the filtrate under reduced pressure. When the viscous residue was triturated with cold water, it solidified and was filtered and dried. It was extracted thoroughly with ethyl ether and filtered. The residual solid appeared to be polymeric. Evaporation of the ether left 1·5 g (4%) of solid which melted at 127°. Extraction of this material with boiling ethylene dichloride dissolved only a trace of product which crystallized from the filtrate when cooled, m.p. 128°. The bulk of material which remained undissolved was extracted with boiling trichloroethane and filtered. Most of the solid again remained undissolved and crystals obtained from the filtrate melted at 134°. The residue was finally dissolved in ether, the solution was cooled in an ice bath and product was crystallized by gradual addition of petroleum ether. This material melted at 136°, and analytical data reported for this compound were obtained from this sample.

(Found: C, 24·71; H, 2·52; N, 32·01. Calc. for $C_7H_6O_9N_8$: C, 24·28; H, 1·73; N, 32·37.)

2,2-*Dinitro-2-Cyanoethanol*

Seventy-six and one half grams of sodium dinitrocyanomethide (0·5 mole) was dissolved in small portions at room temperature in 250 ml of 37% formalin. Twenty-seven and eight-tenths milliliters of chilled concentrated sulfuric acid (0·5 mole) was added with stirring over a ½ hr period. The reaction temperature was maintained between 23 and 26° during this time by means of an ice bath. The reaction mixture was allowed to stand at room temperature for four days and was then extracted with four 50 ml portions of ether. The ether extracts were combined and dried over anhydrous magnesium sulfate. The ether was removed *in vacuo* to yield 76·5 g of 2,2-dinitro-2-cyanoethanol (95% yield). The product was a light yellow liquid, n_D^{20} 1·4470, which solidified on standing overnight in the refrigerator.

2,2-*Dinitro-2-Cyanoethyl Methacrylate*

To 23·8 g (0·113 mole) of trifluoroacetic anhydride and 1·0 g of di-β-naphthol was added dropwise with cooling 9·7 g (0·113 mole) of anhydrous methacrylic acid at such a rate that the temperature did not exceed 30°. The mixture was stirred mechanically at room temperature for 5 min and then 14·0 g (0·087 mole) of 2,2-dinitro-2-cyanoethanol was added dropwise at a temperature of 20–30°. The reaction mixture was stirred for 1 hr and was then poured into 500 ml of ice water. The aqueous mixture was first extracted with a total of 200 ml of ether, and the ether and water layers were then neutralized by the addition of solid sodium bicarbonate. The ether layer was separated and the aqueous layer was extracted with two 50 ml portions of ether. The combined ethereal solution was washed with 50 ml of water and dried over magnesium sulfate. The solvent was removed under reduced pressure to give 15·7 g (79%) of crude ester, which contained a trace of trifluoroacetate as was indicated by its infrared spectrum. The material was flash distilled to yield 6·4 g (32%) of 2,2-dinitro-2-cyanoethyl methacrylate, b.p. 53–58°/0·07 mm. The spectrum of the distillate showed a nitrile absorption band at 2260 cm^{-1}, an ester band at 1740 cm^{-1}, and a dinitrocyanomethyl band at 1602 cm^{-1}.

(Found: C, 36·80; H, 2·91; neut. equiv., 113·5. Calc. for $C_7H_7O_6N_3$: C, 36·69; H, 3·08; neut. equiv., 114·5.)

2,2-*Dinitro-2-Cyanoethyl Acetate*

The procedure described above was used with 27·3 g (0·13 mole) of trifluoracetic anhydride, 7·8 g (0·13 mole) of acetic acid, and 16·0 g (0·10 mole) of 2,2-dinitro-2-cyanoethanol to give 11·3 g (57%) of crude 2,2-dinitro-2-cyanoethyl acetate. Vacuum distillation gave 6·9 g (34%) of product, b.p. 71–92°/1·0 mm. Another fractionation of this material gave 5·2 g (26%) of pure, 2,2-dinitro-2-cyanoethyl acetate, b.p. 73–75°/1·25 mm, n_D^{20} 1·4439, d_4^{20} 1·335.

(Found: C, 30·97; H, 2·45; N, 20·99. Calc. for $C_5H_5O_6N_3$: C, 29·57; H, 2·48; N, 20·69.)

2,2-*Dinitro-2-Cyanoethyl Acrylate*

To 50 ml of chloroform was added 3·5 g (0·022 mole) of 2,2-dinitro-2-cyanoethanol, 1·3 g (0·010 mole) of aluminum chloride, and approximately 1·0 g of *p*-hydroxydiphenylamine. The mixture was stirred mechanically while 1·8 g (0·020 mole) of acrylyl chloride was added with cooling at a temperature of 24–27°. Fifteen minutes after all the acid chloride was added there was no evidence of evolution of hydrogen chloride. The reaction mixture was then heated to 30–35° for 1 hr, and the temperature was increased to 35–40° for an additional hour. After 2 hr of heating rapid evolution of hydrogen chloride had ceased. The mixture was cooled to room temperature, poured into 500 ml of ice water, the chloroform layer separated, and the aqueous layer extracted with three 100 ml portions of chloroform. The chloroform extracts were filtered to remove any aluminum chloride present, and the filtrate was washed with 1% sodium bicarbonate to remove any unreacted acrylyl chloride. After drying the chloroform solution over magnesium sulfate and evaporation of the solvent under reduced pressure, there was obtained 3·2 g (74%) of crude product. Distillation of the material yielded 2·1 g (49%) of ester, b.p. 56–60°/0·1 mm. The distillate, on infrared examination, exhibited a carbonyl absorption band at 1750 cm^{-1} and the expected dinitro-cyanomethyl band at 1600 cm^{-1}.

(Found: C, 32·78; H, 2·21; N, 19·42. Calc. for $C_6H_5O_6N_3$: C, 33·50; H, 2·34; N, 19·53.)

Nitration of 2,2-*Dinitro-2-Cyanoethanol*

To 105 g of mixed acid (42 g of concentrated nitric acid and 63 g of concentrated sulfuric acid) there was added dropwise 12·0 g (0·075 mole) of 2,2-dinitro-2-cyanoethanol at a temperature of 0–5°. After addition of the alcohol, the reaction mixture was removed from the ice-salt bath and allowed to warm to 10°. Oily droplets began to form on the surface of the mixture, which was then poured into 500 ml of ice water. The oily layer was extracted with one 300 ml and two 50 ml portions of ether. The ethereal solution was washed with 50 ml of 1% sodium bicarbonate and three 50 ml portions of water. The ether solution was dried over magnesium sulfate, and the solvent was evaporated under reduced pressure to give 10·3 g (67%) of crude product. A portion of the crude liquid was distilled at reduced pressure to give a colorless liquid, b.p. 46–55°/0·1 mm. The infrared spectrum of this material showed an intense dinitrocyanomethyl band at 1600 cm^{-1} and an intense nitrate ester band at 1678 cm^{-1}.

(Found: N, 24·62. Calc. for $C_3H_2O_7N_4$: N, 27·19.)

2,2-*Dinitro-2-Cyanoethyl Trifluoroacetate*

When 2,2-dinitro-2-cyanoethanol (above) was added to 25 g of trifluoracetic anhydride at 0–5°, the alcohol did not dissolve. The anhydride was heated to reflux and addition of 2,2-dinitro-2-cyanoethanol was continued. The alcohol slowly dissolved under these conditions. The mixture was heated at 55° for another hour and allowed to stand overnight. All volatile material was removed under reduced pressure. The residue was treated with 0·2 g of ethyl centralite and distilled. Three fractions were obtained: (1) 11·3 g, b.p. 33–38°/0·04–0·06 mm, n_D^{20} 1·4037; (2) 1·6 g, 32–39°/0·05–0·08 mm, n_D^{20} 1·4045; (3) 1·9 g, b.p. 80°/0·20–0·24 mm. Fractions 1 and 2 were combined and redistilled yielding a constant boiling fraction, 11·2 g, b.p. 39°/0·15 mm, n_D^{20} 1·4045. The overall yield based on sodium dinitrocyanomethide was 36·6%. The infrared spectrum of this material contained a band at 1812 cm^{-1} attributed to the trifluoroacetyl group, the dinitrocyanomethyl band at 1610 cm^{-1}, and a very weak cyano band at 2260 cm^{-1}.

(Found: C, 23·31; H, 0·53; N, 15·97; sapn. equiv., 129·8. Calc. for $C_5H_2O_6N_3F_3$: C, 23·35; H, 0·78; N, 16·34; sapn. equiv., 128·5.)

2,2-*Dinitro-2-Cyanoethyl Methacrylate*

To 1000 ml of chloroform was added 42·0 g (0·261 mole) of 2,2-dinitro-2-cyanoethanol, 53·5 g (0·40 mole) of aluminum chloride, and 1·5 g of cuprous chloride. The mixture was stirred mechanically while 25·1 g (0·240 mole) of methacrylyl chloride was added with cooling at a temperature of 18–23°. There was no evidence of the evolution of hydrogen chloride. The reaction mixture was heated to 50–60° for 5 hr, then an additional quantity of inhibitor was added before heating seven hours at the same temperature. The mixture was cooled to room temperature, filtered into 2400 ml of ice water, the chloroform layer separated, and the aqueous layer extracted with four 150 ml portions of chloroform. The combined chloroform extract was washed with four 100 ml portions of 5% sodium bicarbonate to remove any unreacted methacrylyl chloride. After drying the chloroform solution over anhydrous magnesium sulfate and evaporating the solvent under reduced pressure, there was obtained 24·2 g (97%) of crude ester. Flash distillation of the crude product yielded 12·9 g (51%), b.p. 62–64°/0·17 mm, n_D^{20} 1·4573.

(Found: C, 37·25; H, 3·32; N, 16·49. Calc. for $C_7H_7O_6N_3$: C, 36·69; H, 3·08; N, 18·34.)

The distillate was flash distilled again to give 11·7 g (47%) of 2,2-dinitro-2-cyanoethyl methacrylate, b.p. 59–62°/0·07–0·10 mm, n_D^{20} 1·4582 and d_4^{20} 1·174. The spectrum was in agreement with that of the previously reported methacrylate prepared via the mixed anhydride technique.

(Found: C, 36·81; H, 3·98; N, 18·63. Calc. for $C_7H_7O_6N_3$: C, 36·69; H, 3·08; N, 18·34.)

Reaction of 2,2-Dinitro-2-Cyanoethanol with Sulfuric Acid and Trioxane

Dinitrocyanoethanol (16·1 g, 0·1 mole) was added dropwise to 50 g of sulfuric acid while the solution was stirred and cooled to maintain the reaction temperature below 60°. When this addition was finished, 3·0 g (0·1 mole) of trioxane was added portionwise to the reaction mixture. After a few minutes of stirring, a white precipitate formed. The reaction mixture was stirred until it cooled to room temperature, was allowed to stand overnight, and was poured onto 150 g of crushed ice; the product was collected on a filter and was washed with water and ethanol. The weight of dried product was 12·5 g. When heated a sample darkened at 180° and decomposed at 220–225°.

The product was insoluble in hot water, hot ethanol, and ether. It was quite soluble in acetone and ethyl acetate. Samples were recrystallized from acetic acid (m.p. 222° dec.), acetonitrile (m.p. 223° dec.), and acetone–ethanol (m.p. 223° dec.). A sample recrystallized twice from acetone ethanol m.p. 224–225° dec., was analyzed.

(Found: C, 28·05; H, 2·88; N, 25·51; M.W., 364; C, 29·45; H, 3·54; N, 21·65.* Calc. for $C_9H_{10}O_{11}N_6$: C, 27·41; H, 2·54; N, 21·32; M.W., 394.)

Alkaline Degradation of Dinitroacetonitrile Derivatives

Reaction of methyl 4,4-dinitro-4-cyanobutyrate with potassium hydroxide

To 1·28 g (0·023 mole) of potassium hydroxide in 15 ml of anhydrous methanol was added dropwise 2·5 g (0·0115 mole) of methyl 4,4-dinitro-4-cyanobutyrate. The resulting 12° rise in temperature was accompanied by immediate precipitation of a yellow material. One hour later there was

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* Different preparation, sample recrystallized twice from acetonitrile, mp 225° dec.

collected on a filter 1·9 g of bright yellow solid which after two recrystallizations from hot methanol melted at 160–161°; on the basis of elemental analysis it appeared to be the potassium salt of methyl 4,4-dinitrobutyrate.

(Found: C, 26·98; H, 3·46; N, 13·16; K, 16·98. Calc. for $C_5H_7O_6N_2K$: C, 26·08; H, 3·06; N, 12·17; K, 16·98.)

Methyl 4,4-Dinitrobutyrate

Eleven and one-half grams (0·05 mole) of the potassium salt of methyl 4,4-dinitrobutyrate (obtained from the alkaline degradation of methyl 4-cyano-4,4-dinitrobutyrate) dissolved in 300 ml of distilled water was neutralized with sulfuric acid. Potassium sulfate was formed immediately and a yellow oil separated as the neutralization proceeded. When the aqueous mixture was definitely acidic, the white precipitate of potassium sulfate had gone back into solution and the oily product had settled to the bottom of the container. One hour later the yellow oil was separated and the aqueous layer was extracted with six 200 ml portions of ether. After addition of the original oily layer to the combined ether extracts, the resulting ethereal solution was washed with five 100 ml portions of distilled water and dried over anhydrous magnesium sulfate. Removal of the drying agent and subsequent evaporation of the solvent under reduced pressure yielded 5·4 g (67%) of crude products. Distillation of a portion of the crude material gave 1·5 g of clear liquid, b.p. 50–51°/0·07 mm, n_D^{20} 1·4542. Infrared spectra of the crude product and the distillate were identical, and the elemental analysis, although a little high for carbon and nitrogen, indicated that the material was methyl 4,4-dinitrobutyrate.

(Found: C, 32·34; H, 4·40; N, 15·34. Calc. for $C_5H_8O_6N_2$: C, 31·25; H, 4·20; N, 14·58.)

The remaining portion of the crude product (approximately 3·9 g) was purified by distillation through a bulb still, head temperature 55–57°/0·04 mm, pot temperature 84–86°, to yield 1·8 g, n_D^{20} 1·4550. Redistillation of this sample through the same apparatus, pot temperature 84–86°, head temperature 46–47°/0·03 mm, gave 1·0 g, n_D^{20} 1·4554. The infrared spectrum of this final distillate was identical with that of the first, and elemental analyses were not made. The molecular weight was determined.

(Found: M.W., 200·3, 201·7. Calc. for $C_5H_8O_6N_2$: M.W., 192·1.)

Reaction of the Sodium Salt of Methyl 4,4-Dinitrobutyrate with Methyl Acrylate

To 4·28 g (0·02 mole) of sodium salt (obtained from reaction of methyl 4,4-dinitro-4-cyanobutyrate with sodium methylate) in 10 ml of distilled water was added 1·70 g (0·0197 mole) of methyl acrylate at 27–31°. The reaction mixture immediately turned dark and a flocculent precipitate separated. After 24 hr the oil which had formed was extracted with four 50 ml portions of ether and the combined ether extract was dried over anhydrous magnesium sulfate. Removal of the drying agent and complete evaporation of the ether under reduced pressure gave 2·4 g of an almost white solid, m.p. 43–45°. When the crude material was dissolved in a minimum of hot ethanol, treated with decolorizing charcoal, filtered, and chilled, there was obtained 2·2 g (40%) of snow-white dimethyl 4,4-dinitropimelate, m.p. 45·5–46·0°.