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CHEMISTRY OF DINITROACETONITRILE—I

PREPARATION AND PROPERTIES OF DINITROACETONITRILE AND ITS SALTS[1]

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Abstract—Two general routes for the preparation of dinitroacetonitrile are known. One method[2] involving reduction of the intermediate trinitroacetonitrile has been modified and improved in both the preparative and degradative steps. Isolation of dinitroacetonitrile as its tetrahydrate, sodium, potassium, silver, ammonium, nitron and tetraphenylarsonium salts is described together with interesting features of solutions of these compounds. Halogenation of dinitroacetonitrile gave chloro- and bromo-derivatives which have been characterized. The occurrence and isolation of the interesting furoxandinitrile as a product of the nitration of cyanoacetic acid is discussed.

DINITROACETONITRILE was first recognized by Schischkoff[3] in 1861 as the parent acid whose ammonium salt was obtained by reduction of trinitroacetonitrile with hydrogen sulfide. Only a preliminary report was made at that time in which was mentioned the isolation of a crystalline, hydrated dinitroacetonitrile by ether extraction of the acidified ammonium salt. Also mentioned were the identities of potassium and silver salts, obtained by neutralizing solutions of the crystalline hydrate, and the presumed identity of a bromo-derivative obtained by bromination of the silver salt. Reconversion of dinitroacetonitrile into trinitroacetonitrile by nitration was recognized. No other account of further work along these lines has appeared in the literature until this time.

Trinitroacetonitrile has been obtained from the nitration with mixed anhydrous acids of such derivatives of cyanoacetic acid as the acid itself, cyanoacetamide, malononitrile and the nitrosated (oximino) and mono- and dinitro derivatives of each of these (where known). It is presumed that trinitroacetonitrile survives as an end product of rather vigorous nitrating conditions because the three nitro groups effectively drain electrons away from the cyano-group making it resistant toward attack by electrophilic species. The induced positive character of the cyano-group was indicated by its vulnerability toward attack by nucleophilic species including water. Hydrolysis by water during its preparation was minimized by using an oleum containing enough SO_3 to convert all water formed in the reaction to sulfuric acid. Isolation of crystalline trinitroacetonitrile required exposure of personnel to hazards related to its friction and impact sensitivity and its very noxious and toxic vapors. Therefore, a very considerable improvement in the safety aspects and convenience of synthesis of

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[1] This research (Parts I to IV) was carried out under Army Ordnance Contract DA-01-021-ORD-5135

[2] A second method is described in the fourth paper of this series, *Tetrahedron* 17, 109 (1962)

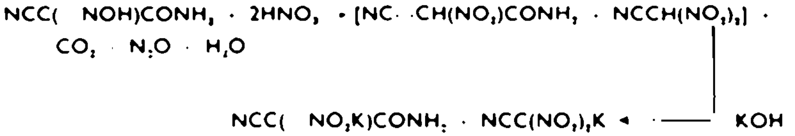
[3] I. Schischkoff, *Liebigs Ann.* 119, 250 (1861); *Beil* 2, 228

trinitroacetonitrile was realized by carrying out the nitration reaction in the presence of carbon tetrachloride. In CCl_4 solution trinitroacetonitrile could be manipulated safely, assayed and stored or used directly for the preparation of dinitroacetonitrile derivatives.

Cyanoacetic acid was found to be the most satisfactory starting material for the preparation of trinitroacetonitrile. Comparisons of the effect on yield of variations in the ratios of reagents indicated that optimum proportions were very nearly stoichiometric as given by equation (1).

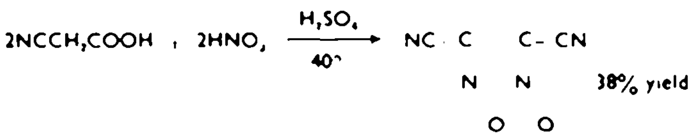
$$NC{-}CH_2{-}COOH + 3HNO_3 + 3SO_3 \xrightarrow{(CCl_4)} (73\text{–}77\%)NCC(NO_2)_3 + CO_2 + 3H_2SO_4 \quad (1)$$

Preparation of dinitroacetonitrile by direct nitration of cyanoacetic acid was investigated by varying the ratio of reagents and reaction conditions. Interpretation of the results of these experiments was predicated upon detection of dinitrocyanomethide ion as the easily purified potassium salt (See Experimental). In no case could this ion be detected by non-reductive neutralization of reaction mixtures. Apparently whatever intermediates intervene in the conversion of cyanoacetic acid to trinitroacetonitrile are transitory in nature and do not accumulate in the reaction mixtures. However, when oximinocyanoacetamide was treated with less than equivalent quantities of nitric acid and the reaction mixture was quenched and neutralized with potassium hydroxide, it was possible to separate and to identify the components as salts of fulminuric acid (nitrocyanoacetamide) and dinitroacetonitrile.



$$NCC(=NOH)CONH_2 + 2HNO_3 \rightarrow [NC{\cdot}CH(NO_2)CONH_2 + NCCH(NO_2)_2] + CO_2 + N_2O + H_2O$$
$$\xrightarrow{KOH} NCC(=NO_2K)CONH_2 + NCC(NO_2)_2K \quad (2)$$

When the mole ratio of nitric acid to cyanoacetic acid was reduced to the vicinity of 2:1 to 1:1 and the amount of sulfuric acid was reduced to catalytic proportions, a new product could be isolated from the reaction mixtures in low yields. This material curiously resembled trinitroacetonitrile closely in appearance, odor and melting point. It was identified as 3,4-dicyanofuroxan[4] by hydrolysis to furoxan-3,4-dicarboxamide.[5] This simple one-step nitration of cyanoacetic acid appears to offer a convenient synthesis of an interesting furoxan derivative which has not been fully investigated.



$$2NCCH_2COOH + 2HNO_3 \xrightarrow[40^\circ]{H_2SO_4} NC{-}C{=}C{-}CN \ (\text{furoxan ring: } N{-}O{-}N{\to}O) \quad 38\%\ \text{yield} \quad (3)$$

The reduction of trinitroacetonitrile to dinitroacetonitrile has been effected by numerous reducing agents. Schischkoff used hydrogen sulfide, which was reported to react according to equation (4). Bromide ion was found to function effectively in an acidic ethanol medium. The mechanism and details of this reaction were never fully

$$C(NO_2)_3CN + 4H_2S \rightarrow NH_4^+\,C(NO_2)_2CN^- + 4S + 2H_2O \quad (4)$$

elucidated. Neutralization of the entire reaction mixture with various bases gave satisfactory yields of dinitrocyanomethide salts. Contamination by the corresponding

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[4] C. Ulpiani, *Gazz. Chim. Ital.* 42, 1243 (1912). *Chem. Abstr.* 6, 2235 (1912).

[5] H. Wieland and E. Gmelin, *Liebigs Ann.* 367, 80 (1909).

trinitromethide salt was minimized if sufficient ethanol and a low enough pH were employed. Sulfur dioxide was found to be serviceable for the replacement of the bulk, but not all of the hydrobromic acid.

For synthetic purposes, sodium dinitrocyanomethide was found to be the most generally useful salt for isolation from the reaction mixture since all other derivatives could be prepared from it. Potassium dinitrocyanomethide was much easier to isolate and to purify due to its sparing solubility in most solvents. (See Table 1.) However, from solutions (usually suspensions) of potassium dinitrocyanomethide attempts to prepare other dinitrocyanomethide salts by metathesis, to isolate dinitroacetonitrile tetrahydrate by acidification with mineral acids or to obtain halodinitrocyanomethyl derivatives were unsuccessful and unreacted potassium salt could be recovered. When reactions were found which did proceed using potassium dinitrocyanomethide, viz., nitration with absolute nitric acid which gave trinitroacetonitrile, dissolution in excess formalin solution which gave some dinitrocyanoethanol[6] and a sulfonic acid ion exchange column[7] which retained all potassium ions and gave an effluate containing dinitroacetonitrile tetrahydrate, it was realized that the unsuccessful reactions failed because of unfavorable equilibrium conditions due to the low solubility of potassium dinitrocyanomethide and the ionic character of the dinitrocyanomethide ion. Other reagents which reacted with potassium dinitrocyanomethide attacked the dinitrocyanomethide ion, as for example, hot aqueous alkali, which gave potassium dinitrothane and alcholic hydrogen chloride which converted it to dinitroacetamide.[8]

TABLE 1. SOLUBILITY OF SODIUM AND POTASSIUM DINITROCYANOMETHIDE AT 25

Solvent	Potassium Dinitrocyanomethide (g/100 g of solution)	Sodium dinitrocyanomethide (g/100 g of solution)
Ethanol	0.09	31.8
Ethyl acetate	0.06	31.5
Acetone	5.97	51.1
Diethyl ether	< 0.01	< 0.01
Water	4.11	> 60

The unusual properties of potassium dinitrocyanomethide appear to be derived principally from the equally striking character of the dinitrocyanomethide ion.[9]

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[6] Part II. C. O. Parker, W. D. Emmons, A. S. Pagano, H. A. Rolewicz and K. S. McCallum, *Tetrahedron* 17, 89 (1962).

[7] Rohm & Haas Company Amberlite IR-120.

[8] Part III. C. O. Parker, *Tetrahedron* 17, 105 (1962).

[9] Nitroform has an acid strength approximating that of phosphoric acid, the yellow color of aqueous-nitroform solutions is readily discharged by addition of mineral acids. It may be presumed that the trinitromethide ion is sterically unable to acquire a planar configuration so that contributions of all possible polar structures to resonance stabilization of the trinitromethide ion are not fully realized. Consequently, only limited resonance energy is lost by the ion in going to covalent trinitromethane.

Sharp contrast is noted with every point of comparison to dinitroacetonitrile. Dinitrocyanomethide salts are very stable thermally compared to trinitromethide salts. No repression of ionization of dinitroacetonitrile solutions by mineral acids could be observed. Covalent dinitroacetonitrile apparently does not exist; instead there was obtained what amounts to a crystalline, solvated dinitrocyanomethide ion, i.e. dinitroacetonitrile tetrahydrate. Finally, solution reactions of dinitrocyanomethide salts gave products derived from all polar structures which might contribute to resonance stabilization of the dinitrocyanomethide ion. (See paper II, this series.) These facts suggest that the best explanation for the distinguishing chemical properties of dinitroacetonitrile may be ascribed to the unique co-planarity and resonance stabilization of the dinitrocyanomethide ion.

Molecular weight and conductivity measurements showed the sodium and potassium salts to be completely ionized in aqueous solution. The equivalent conductances obtained at infinite dilution were 123 ohm^{-1} for the potassium salt, 98 ohm^{-1} for the sodium salt, and 226 ohm^{-1} for the silverpotassium salt. When the equivalent conductances of the cations were subtracted from these values, the conductances at infinite dilution for the dinitroacetonitrile anion in each salt were 49 ohm^{-1}, 48 ohm^{-1}, and 45 ohm^{-1}, respectively. Neither salt could be titrated potentiometrically with perchloric acid in acetic acid solution, which distinguishes them from nitrate salts, for example, and indicates that dinitroacetonitrile is a stronger acid than nitric acid.

TABLE 2. MOLAR EXTINCTION COEFFICIENT × 10^{-3}[a]

millicrons, mμ	220	232	250	256	288	345	398
Max		7.3		7.0		15.6	
Min	5.4[b]		6.6		1.4		0.5[c]

[a] Potassium dinitrocyanomethide; all values only approximate, taken from a condensed reproduction.
[b] Cut-off.
[c] Tail-off.

The pH of the solution had an inappreciable effect on the dissociation of dinitroacetonitrile, as evidenced by indistinguishable ultraviolet absorption spectra of dinitrocyanomethide salts whether measured in water or in 20 per cent aqueous sulfuric acid solution.

Other dinitrocyanomethide salts which could be prepared by metathesis with aqueous solutions of the sodium salt containing the appropriate cation were: (Melting-decomposition point in parenthesis) Na. anhyd. (226°), K (268°), NH_4(182°), Ag (196°), nitron (189°) and Ph_4As (177°). From solutions of potassium dinitrocyanomethide containing silver ions a silver-potassium double salt crystallized upon cooling, m.p. 224°. The 1:1 mole ratio of silver to potassium in the salt which crystallized was unaffected by the solvent. Halide ions precipitated the silver.

Dinitroacetonitrile itself was never isolated in pure, anhydrous condition. However, hydrated dinitroacetonitrile fortuitously showed appreciable solubility in ethyl ether and from ether solutions colorless crystalline products could be isolated. The melting point of this material varied from 37–40° depending upon the preparation; it was insoluble in non-polar solvents and gave neutral equivalents, elementary analyses, and water determinations (Karl Fischer) which were in agreement with several dinitroacetonitrile hydrates. The amount of water present varied somewhat, but each preparation gave good analytical data, water analysis, and neutral equivalent for a particular hydrate. All samples contained three to four moles of water per mole of dinitroacetonitrile. Attempts to remove the water gave crude products having neutral equivalents ranging down to 144 (pure dinitroacetonitrile, 131). Distillation of dinitroacetonitrile hydrate, under reduced pressure produced in part, decomposition to nitric acid. The crystalline tetrahydrate was quite stable when kept cold, and no loss of water took place after five days evacuation over phosphorous pentoxide at 0°. On the other hand, samples stored at room temperature at atmospheric pressure softened and discolored within two days. Sodium dinitrocyanomethid itself formed a stable monohydrate (m.p. 214–216°) on exposure to normal laboratory atmosphere (50 per cent relative humidity). Although anhydrous dinitroacetonitrile could not be islolated as such, essentially anhydrous solutions of dinitroacetonitrile in various solvents were prepared by neutralizing suspensions of anhydrous sodium salt with an equi-molar quantity of sulfuric acid. Such solutions were stable enough for immediate synthetic use. All of the aforementioned properties of dinitroacetonitrile, its existence as a crystalline hydrate and its instability when the water of hydration was removed, its apparent complete dissociation in strong mineral acid solution, strengthen the impression that dinitroacetonitrile would best be represented as hydronium dinitrocyanomethide.

TABLE 3 MOLECULAR WEIGHTS OF SODIUM AND POTASSIUM DINITROCYANOMETHIDE

Salt	$NaC(NO_2)_2CN$	$KC(NO_2)_2CN$
Theor mol wt. (2 ions per mole)	76.5	84.5
Cryoscopic in water	75.5	83.9
Ebullioscopic in water	75.3	88.9
Ebullioscopic in acetone	104.0	116.1
Fraction dissociated in acetone	0.74	0.73

The only covalent derivatives of dinitroacetonitrile to be considered in this paper are the nitro- and halogen-derivatives; others are described in the succeeding papers. Trinitroacetonitrile as mentioned above, could be obtained rather easily by nitration of dinitroacetonitrile or its salts. A sort of autonitration or disproportionation reaction was observed to take place when dinitroacetonitrile tetrahydrate was suspended in excess cold, concentrated sulfuric acid and cold, fuming sulfruic acid was added: trinitroacetonitrile slowly sublimed away from the liquid phase and condensed on the vessel walls. Nucleophilic attack on trinitroacetonitrile has been observed to take place in two ways: hydroxide ion, which requires a very high oxidation potential, appears to attack the cyano-group and give trinitromethide salts and cyanate ion in good yield, depending on the conditions. More easily oxidized agents (or media) may be presumed to undergo a one-electron transfer to give the very stable dinitrocyanomethide ion.

The halogen derivatives, chloro- and bromo dinitroacetonitrile, were prepared readily by halogenation of solutions of sodium dinitrocyanomethide. A superior method of preparation of chlorodinitroacetonitrile was found to consist in oxidation of solutions of sodium dinitrocyanomethide in hydrochloric acid with hydrogen peroxide, thereby avoiding contamination of the chloroderivative with much excess free chlorine. Application of this method to the preparation of the bromo-derivative was never attempted. Investigation of the chemistry of these compounds was very limited. Attempts to bring about addition of bromodinitroacetonitrile to ethylene and to cyclohexene failed to yield dinitrocyanomethyl adducts.

EXPERIMENTAL

Trinitroacetonitrile[10]

Cyanoacetic acid, 340 g (4 moles), was suspended in 1000 ml of carbon tetrachloride in a 12 l., three-necked, round-bottom flask equipped with a thermocouple, a mechanical stirrer, a 1 l. funnel and a Dry Ice cooled condenser. The latter two items were attached to the flask by means of a 'Y' tube and each was protected from atmospheric moisture by means of a calcium chloride drying tube. The contents of the flask were cooled to 0 C, and 630 ml (13.5 moles) of white fuming nitric acid, d 1.49-1.50, was introduced rapidly by means of the addition funnel. Seven hundred and fifty milliliters of 27% fuming sulfuric acid (16 moles) were poured into the addition funnel and then with a Dry Ice-isopropanol bath strategically placed beneath the flask, the entire quantity of acid was added by remote control as rapidly as it would flow from the funnel (usually about 5-6 min) while the temperature of the reaction mixture was maintained below 10. The temperature of the reaction mixture was allowed to rise to 25° and was kept at this level for 80 min. It was then allowed to rise to 30° where it remained for about ½ hr by spontaneous, but slow, evolution of heat. The mixture was then cooled to about 10° and poured into a 3 l. separatory funnel. The lower, mixed acid layer was separated from the carbon tetrachloride layer and extracted with a 300 ml portion of carbon tetrachloride. The carbon tetrachloride solutions were combined and shaken with two 250 ml portions of ice cold 70% sulfuric acid. On separation from the last of these acid solutions, a colourless to light yellow carbon tetrachloride solution of trinitroacetonitrile (73-77% yield) was obtained. When the solution was to be stored for an extended period of time, about 25 g of anhydrous magnesium sulfate was added to the solution to insure desiccation.

TABLE 4. TIME REQUIRED FOR HYDROLYSIS OF TRINITROACETONITRILE

Sample No	Concentration of trinitroacetonitrile (g/100 ml.) determined after ¼ hr	½ hr	1 hr
1	25.5	25.7	25.5
2		25.7	25.5

TABLE 5. GRAMS TRINITROACETONITRILE FOUND PER 100 ml OF SOLUTION

Sample no.	Gravimetric method	Ultraviolet method	Infrared method
1	23.14	23.0	23.3
2	30.22	30.1	30.8
3	32.88	32.6	33.3
4	24.97	24.3*	25.3
5	26.08	25.9	26.6
6	23.84	23.6	23.6

* This figure is the average of four measurements, all others are the average of two measurements.

Analysis of Trinitroacetonitrile

The best results were obtained when trinitroacetonitrile in carbon tetrachloride solution was hydrolyzed by stirring with excess aqueous alkali for approximately 15 min (Table 4). The trinitromethide

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[10] *Warning*

All manipulations of trinitroacetonitrile, trinitromethyl and dinitrocyanomethyl derivatives were performed either remotely (quantities greater than 25 g) or from behind the protection of safety shields tested for resistance to detonation of 25 g charges of explosive at distances of not less than eight inches. The same precautions were observed with storage of samples. All melting point baths were enclosed in Plexiglas cabinets, since rupture of a melting point apparatus occurred more than once. All personnel were required to wear safety glasses with side guards upon entering the laboratory area.

salt was then determined either gravimetrically with tetraphenylarsonium chloride or by measuring the optical absorption of an appropriate dilution at 350 mμ.

An alternative, very rapid method was based on measuring the optical absorption of the nitrile band at 2250 cm^{-1}. This method allowed direct use of the carbon tetrachloride solution or a singly diluted solution. Table 5 shows the agreement obtained with these three methods.

The gravimetric procedure was believed to be the most precise because the per cent error involved in weighing is very much less than that involved in the spectrophotometric methods. The infrared method was certainly the fastest and probably the least sensitive to contaminants.

As regards the determination of trinitromethide ion using tetraphenylarsonium chloride, the effect of varying the volume of solution from which the tetraphenylarsonium trinitromethide is precipitated was studied. Changes of volume between 20 ml and 155 ml were without significant effect on the results.

The precision of the gravimetric procedure was tested by analysis of ten aliquots from a single nitroform solution. Results ranged from 97·64% to 100·82%, average 98·45%, standard deviation 1·05% based on the weighed nitroform. Since this work was done during the familiarization period, it is expected that the method is capable of more precise results.

The precision of the ultraviolet absorption method could probably be improved by a differential measurement using a standard solution for the initial instrument setting. Potassium trinitromethide was first tried as a standard solution. Solutions of the order of 10^{-3} molar were found to be stable for two weeks; stronger solutions were quite unstable. Solid ammonium trinitromethide and aqueous 0·1 and 0·01 M solutions of ammonium trinitromethide were stable for at least three weeks within the limits of detection by ultraviolet absorption.

Sodium Dinitrocyanomethide

To a mechanically stirred solution of 600 ml of 48% hydrobromic acid in 1700 ml of ethanol contained in a three-necked, 12 l. flask was added a solution of trinitroacetonitrile (the total product of a 4 mole run) in approximately 1600 ml of carbon tetrachloride. The temperature of the reaction mixture slowly increased to about 50–55°, and remained there for approximately 1 hr. During this time the solution became red, then brown, and finally black; brown fumes resembling bromine were quite evident. It has also been observed that ethyl nitrite is one of the major by-products of this reaction, and therefore adequate ventilation must be provided in the vicinity of the reaction vessel. When the evolution of heat ceased, the solution was cooled to 0–5° and was neutralized with sufficient 3 N methanolic sodium hydroxide to raise the pH value to 8. Addition of base caused the solution gradually to become red, orange, and finally at the desired pH value, a very light yellow. A small quantity of precipitated sodium bromide usually made its appearance during the neutralization step. The solvent was then distilled from the reaction mixture at reduced pressure and the dry residue was extracted with two 500 ml portions of ethyl acetate. The ethyl acetate solution of sodium dinitrocyanomethide was treated with decolorizing charcoal and the salt was precipitated by addition of 2 l. of ether. The sodium dinitrocyanomethide, 360–400 g (59–65%), was separated by filtration and dried in a vacuum oven at 70–80° for 4 hr. Its melting point (decomposition) was 224–226°.

(Found: Na, 13·96. Calc. for $\mathrm{NaC(NO_2)_2CN.\ H_2O}$, m.p. 214–216°, recrystallized from ethyl acetate benzene solution: Na, 13·45.)

(Found: Na, 15·36. Calc. for $\mathrm{NaC(NO_2)_2CN}$: Na, 15·03.)

Potassium Dinitrocyanomethide

The preparation of potassium dinitrocyanomethide was identical with that of the sodium salt with the exception that methanolic potassium hydroxide was substituted for sodium hydroxide. The work-up of the salt was considerably simplified by the fact that potassium dinitrocyanomethide was insoluble in the solvent system in which it was formed. Potassium dinitrocyanomethide and potassium bromide, which was equally insoluble, were isolated on a filter.[11] The mixture of salts (800–900 g) was dried for 6 hr at 70–80° in a vacuum oven and then transferred to a 1500 ml Soxhlet extractor and extracted with 2 l. of acetone over a 12 hr period.

Most of the potassium dinitrocyanomethide, which is only moderately soluble in acetone, was

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[11] This salt mixture could be triturated with cold water, refiltered, washed with cold water and the filter cake recrystallized from water without losing prohibitive quantities of the potassium dinitrocyanomethide originally present.

filtered from the acetone in the distillation flask at this time. The balance was precipitated by the addition of about 1 l of ether to the acetone solution which had been previously concentrated to one-fourth of its original volume. By this procedure there was obtained 455–500 g (67–75%) of potassium salt which melted with decomposition at 262–264°.

Crude salt recrystallized from water exhibited a yellow color. It could be suspended in 85% phosphoric acid and stirred overnight, filtered, washed with ethanol and recovered in pure, white condition. The same treatment using concentrated hydrochloric acid or recrystallization from 20% aqueous sulfuric acid also helped remove yellow coloration.

(Found: K, 22·99. Calc. for $C_2O_4N_3K$: K, 23·12.)

Silver-Potassium Dinitrocyanomethide Double Salt

Potassium dinitrocyanomethide was dissolved in an aqueous solution containing a two-fold excess of silver nitrate. The product which crystallized on cooling the solution was recrystallized from fresh aqueous silver nitrate solution and then twice from distilled water, m.p. 224°. When this product was dissolved in acetone and precipitated by the addition of ether, the silver content was unchanged.

(Found, Ag, 26·48. Calc. for $C_4O_8N_6AgK$: Ag, 26·51.)

Dinitroacetonitrile Polyhydrate

Thirty-two and four-tenths grams of sodium dinitrocyanomethide (0·211 mole) was dissolved in 17·5 ml of water, and the water layer was covered with 60–70 ml of ether. The mixture was stirred in a cooling bath and 20·7 g (0·21 mole) of concentrated sulfuric acid was added dropwise. There was no resulting aqueous layer, and the ether was decanted from the moist salt. Extraction with ether was continued in portions until the extracts became colourless. The ether extracts were dried overnight with anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The residual crystalline solid was washed onto a filter with methylene chloride. After evacuation in a desiccator there was obtained 25·3 g of white crystals m.p. 37–40·5°. The water content of this material was determined by Karl Fisher titration.

(Found: Neut. equiv., 186·7, H_2O, 31·0. Calc. for $C_2HN_3O_4 \cdot 3{\cdot}25H_2O$: Neut. equiv., 188·5; H_2O, 31·1.)

When a similarly prepared product was transferred from the filter directly to a flask and was sublimed at 20°/1·0 mm, a white crystalline product was obtained in an ice-cooled receiver. This sublimate had the composition of a tetrahydrate, m.p. 37–40°.

(Found: C, 12·42; H, 4·26; N, 19·89; neut. equiv., 202·0. Calc. for $C_2HN_3O_4 \cdot 4H_2O$: C, 11·82; H, 4·43; N, 20·69; neut. equiv., 203·1.)

Continued distillation of the residue (treated with 1% diphenylamine) gave a liquid fraction. This was redistilled twice and was finally found to be mostly nitric acid, as indicated by the melting point of its nitron derivative (m.p. 263°).

All preparations of the initial crystalline product, whether the mineral acid employed was sulfuric, hydrochloric, or phosphoric acid, yielded nitron derivatives which, after recrystallization from ethanol, melted at 189–190°, and gave no depression in melting point when mixed with a derivative prepared directly from samples of crystalline hydrate which had liquefied after evacuation overnight in the presence of concentrated sulfuric acid. Distillation of this liquefied material, however, produced decomposition even at low temperatures.

Silver Dinitrocyanomethide

A solution of 116·2 g (15% molar excess) of silver nitrate in 40 ml of water was added to a solution of 70·5 g (0·46 mole) of sodium dinitrocyanomethide in 80 ml of water at 40°. The suspension of silver salt was cooled, filtered and washed with cold ethanol. The product was recrystallized from 300 ml of water heated to 90° and filtered while hot, giving 67·4 g (61·5% yield) of silver dinitrocyanomethide. The salt exploded at 196° in a capillary melting point tube and shattered the apparatus. It is soluble in acetonitrile, water and acetone and insoluble in alcohols.

(Found: Ag, 44·92. Calc. for $C_2O_4N_3Ag$: Ag, 45·33.)

Bromodinitroacetonitrile

Sodium dinitrocyanomethide (9·0 g, 0·059 mole) was dissolved in a mixture of 9 ml of water and 13 ml of methylene chloride. Calcium carbonate (5 g) was suspended in the mixture, which was stirred vigorously at 0–5°. Bromine (3 ml, 0·059 mole) was added to the mixture dropwise. The organic layer was separated and dried with magnesium sulfate. After removal of drying agent and solvent, the residue was distilled and two fractions were collected: (1) 1·6 g, 40°/5–10 mm, n^{25} 1·4832; (2) 2·7 g (22%), 35–36°/4 mm, n_D^{25} 1·4860. Fraction (2) was titrated iodimetrically and found to contain 96% bromodinitroacetonitrile (positive bromine). The infrared spectrum of this material contained nitrile and dinitrocyanomethyl absorption bands at 2240 cm^{-1} and 1608^{-1}, respectively.

Chlorodinitroacetonitrile

Thirty-three grams (0·19 mole) of sodium dinitrocyanomethide monohydrate was added in one portion to a stirred mixture of 70 ml of concentrated hydrochloric acid and 70 ml of 30% hydrogen peroxide at 30°. The reaction temperature was maintained at 33–35° for 2 hr by the intermittent application of an ice bath. During this interval, a colorless oil separated from the solution. The mixture was cooled to about 5° and the two layers separated. The product was washed once with a 15 ml portion of water and was dried over calcium chloride to yield 30·8 g of chlorodinitroacetonitrile. The product rapidly became yellow on standing at room temperature. Distillation of the crude product (b.p. 38°/14 mm) yielded 29·0 g (91%) of chlorodinitroacetonitrile, n_D^{20} 1·4509.

3,4-*Dicyanofuroxan*

Seventeen grams (0·2 mole) of cyanoacetic acid was dissolved in 50 ml of trifluoroacetic acid magnetically stirred in a 250 ml three-necked flask equipped with a thermometer, drying tube-closed water condenser and a stoppered, pressure-equalized 25 ml dropping funnel. Fifteen and eight-tenths grams (0·25 mole) of anhydrous nitric acid was placed in the dropping funnel. The reaction mixture was warmed to 40° and slow dropwise addition of the nitric acid was begun. After 1 ml had been added, 0·5 ml of 30% fuming sulfuric acid was added from a pipette through the condenser. About 2 hr elapsed during the addition of nitric acid, during which time the reaction temperature was held at 40° ± 5°. Soon after the acid was all added the solution was cooled and poured with stirring over 200 g of ice and water. The quenched mixture was extracted with two 20 ml portions of methylene chloride. The combined extracts were washed with cold water until neutral and dried with sodium sulfate. Solvent was evaporated and the residue (which is rather volatile) was triturated with carbon tetrachloride, causing it to crystallize. The white crystals were filtered, washed with cold carbon tetrachloride and recrystallized from just enough carbon tetrachloride to give a solution at 40°. Cooling this solution gave 5·2 g (38% yield) of crisp, white product, m.p. 42°. The product sublimed rapidly onto a Dry Ice cooled cold finger when heated to 35°/0·1 mm. Its infrared spectrum contained clean, sharp bands at the following frequencies, all of which, except the cyano-(2227 cm^{-1}) correspond to characteristic vibrations of the furoxan ring recognized by Boyer *et al.*[11] 2227, 1637, 1460, 1305, 1104, 1045, 844, 745, 688 cm^{-1}, (capillary melt spectrum). Elementary analysis of this material ($C_4O_2N_4$) gave consistently low values for nitrogen which made the analysis valueless.

Furoxan-3,4-*Dicarboxamide*

Four-tenths grams of sublimed dicyanofuroxan was dissolved in 5 ml of concentrated sulfuric acid at room temperature and the solution was left idle overnight. The colourless solution was poured onto 25 g of crushed ice causing precipitation of white solid material. The product was collected on a filter, washed with ice-water until the washes were neutral and recrystallized from hot water, m.p. 233°.[12]

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[11] N. E. Boyer, G. M. Czerniak, H. S. Gutowsky and H. R. Snyder, *J. Amer. Chem. Soc.* 77, 4238 (1955).

[12] H. R. Snyder and N. E. Boyer, *J. Amer. Chem. Soc.* 77, 4233 (1955), report m.p. 232°.