some form, in complex I. Thus complex I cannot be formed, whatever the nickel:DMGOH ratio, unless ammonia is present in solutions. When solutions of complex I are stripped of ammonia by diffusion, etc., the complex decomposes before the ammonia is completely removed. When primary amines, *e.g.*, monoethylamine, are used instead of ammonia a compound similar to complex I is produced having an absorption spectrum almost identical with complex I except that the peak at 530 mμ found with complex I, is altered in shape and size and it is to be inferred that this absorption arises from an ammonia group in the molecule. It is also significant that only ammonia will give complex I from Edelman's black solid.[7]

Discussion

The experimental data given above are mutually consistent and lead to the equation of formation of complex II to be given as

$$Ni^{2+} + 4DMGOH + 6OH^- \longrightarrow [Ni(OH)_2(DMGO)_4]^{1-} + 4H_2O + 3e^-$$

with the compound having the empirical formula shown. However its structure remains to be determined. The valency of the nickel is also uncertain, although it seems likely that one electron is removed in raising Ni^{II} to Ni^{III} and the other two are removed from the two hydroxyl groups. The very high molecular extinction coefficient of this compound would indicate resonance.

It would be logical to assume complex I to be an analogous compound with amino groups replacing two of the four dimethylglyoxime groups, but in the absence of evidence of the number of ammonia molecules involved this cannot be verified.

Complex I is formed almost exclusively in all published analytical methods but it would be much better to use complex II, as the former is unstable and can either decompose or partially revert to complex II in a comparatively short time. To achieve rapid and quantitative formation of complex II a good initial excess of dimethylglyoxime should always be present with only the minimum amount of oxidant (2–3 ml. of 0.01 *N* iodine or bromine), so that excess dimethylglyoxime is not oxidized before it can convert any complex I to II. The ammonia present in solutions should be kept to a minimum and the correct alkalinity (pH > 11) obtained by adding sodium hydroxide.

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Condensations of Primary Aliphatic Nitramines with Formaldehyde

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In the course of some studies of the chemistry of primary aliphatic nitramines we have observed a convenient condensation of formaldehyde with several primary nitramines in strong sulfuric acid leading to the formation of N,N′-dialkylmethylenedinitramines.

$$2RNHNO_2 + CH_2O \xrightarrow{ca.\ 90\%\ H_2SO_4} [RN(NO_2)]_2CH_2 + H_2O \quad (I\text{–}IV)$$

I, R = CH_3
II, R = C_2H_5
III, R = n-C_4H_9
IV, R = $-CH_2-$

Thus formaldehyde seems to stabilize the primary nitramines to strong sulfuric acid. Holstead and Lamberton[1] have recently noted a quite analogous reaction (equation A) in which intermediately formed formaldehyde and nitramide (NH_2NO_2) condense with acetanilide under similar conditions.

$$AcO[CH_2N(NO_2)]_3CH_2OAc \xrightarrow[\text{concd. } H_2SO_4]{C_6H_5NHAc} (p\text{-}AcNHC_6H_4CH_2)_2NNO_2 \quad (A)$$

The yields from the condensation reaction are only fair, probably due to the concurrent decomposition of the nitramines in the strong acid.[2] Since low temperatures (below 0°) and very efficient stirring were found to be necessary for good results, *ca.* 90% sulfuric acid solutions were used to permit these conditions. A complete study of the reaction variables was not made and the listed yields are probably not optimum. Compound IV was more conveniently prepared by the cyclization of the monomethylol derivative of ethylenedinitramine[3] in the strong sulfuric acid solution. The methylol derivatives of primary aliphatic mononitramines are unknown, probably due to an unfavorable equilibrium.[4]

Cyclohexyl nitramine failed to react similarly to the other primary nitramines and it was not found possible to identify any products from the reaction. Nitrourethan also failed to condense with formaldehyde under the chosen experimental conditions and could be recovered from the acid solution. The very low basicity of the compound probably prevents the condensation. Attempts to employ chloral or paraldehyde in place of formaldehyde were unsuccessful.

The use of the Lewis acid, boron trifluoride, as a substitute for the sulfuric acid is briefly noted in the experimental section.

Compounds III and IV showed the typical secondary nitramine ultraviolet spectrum[5] having λ_{max} 240 mμ(ϵ 11,300) and λ_{max} 235 mμ (ϵ 11,500), respectively, when measured in absolute ethanol.

Compounds (I–IV) appear to be useful intermediates in the synthesis of some substituted hydrazines and experiments, with this object in mind, are in progress.

Experimental[6]

The primary mononitramines were prepared by nitration of the appropriate N-alkyl urethans,[7] ammonolysis, in dry

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(5) R. N. Jones and G. D. Thorn, *Can. J. Research*, **27B**, 828 (1949).

(6) Melting and boiling points are not corrected.

(7) H. M. Curry and J. P. Mason, THIS JOURNAL, **73**, 5043 (1951)

ether, of the nitrourethans, and acidification of the resulting ammonium salts. Nitrourethan was prepared by a slight modification of the direct nitration of Brian and Lamberton[8] in which the nitration mixture was drowned in ice-water and then ether-extracted directly to give a 97% yield of product.

Ethylenedinitramine, (EDNA), was prepared from 2-imidazolidone according to the directions of Bachmann, *et al.*[3b]

2,4-Dinitro-2,4-diazapentane (I). (A).—To a solution of 2.5 g. of paraformaldehyde in 160 ml. of 90% (by weight) sulfuric acid, chilled in an ice–salt-bath (−2 to −6°), was added, in small portions and with vigorous stirring, 9.0 g. of methylnitramine. The solution was stirred about 10 minutes after the addition and was then poured onto a large quantity of ice. On standing 1.7 g. of material, m.p. 41–44°, slowly precipitated. Ether extraction of the filtrate gave a further 2.1 g. of product melting at 48–50.8°. These combined products represent a 39% yield. By recrystallization from a chloroform–hexane mixture an analytical sample, melting at 49.2–50.9°, was realized.

Anal. Calcd. for $C_3H_8N_4O_4$: C, 21.95; H, 4.91; N, 34.14. Found: C, 22.11, 21.92; H, 4.86, 4.79; N, 33.99.

(B).—A mixture of 1.5 g. of methylnitramine, 0.4 g. of paraformaldehyde, 16 ml. of trifluoroacetic anhydride and 10 drops of boron trifluoride etherate was stirred 2.5 hours with ice-bath cooling. After standing overnight in the refrigerator the mixture was poured onto ice, neutralized with sodium bicarbonate and ether extracted. The ether was dried over magnesium sulfate and was evaporated, leaving 0.3 g. of a brown oil which could not be induced to crystallize. The oil was dissolved in 10 ml. of chloroform, poured onto a one cm. (10 g.) column of activated alumina, and eluted with 40 ml. of chloroform. The eluate solidified on long standing.

Anal. Calcd. for $C_3H_8N_4O_4$: N, 34.14. Found: N, 33.97.

On recrystallization from chloroform–hexane the melting point was 49–51° and there was no melting point depression when mixed with the material from method (A).

3,5-Dinitro-3,5-diazaheptane (II).—To a solution of 0.7 g. of paraformaldehyde in 50 ml. of 90% sulfuric acid was added 3.0 g. of ethylnitramine as in method (A) for compound I. The drowned reaction mixture deposited 1.7 g. of a white solid melting at 74–77° and ether extraction of the filtrate gave 0.2 g. of solid for a total yield of 43%. An analytical sample, m.p. 75.7–77.2°, was realized by crystallization from hexane.

Anal. Calcd. for $C_5H_{12}N_4O_4$: C, 31.25; H, 6.30; N, 29.15. Found: C, 31.24, 31.31; H, 6.35, 6.28; N, 29.36, 29.48.

5,7-Dinitro-5,7-diazaundecane (III). (A).—Over a 40-minute period 8.4 g. of *n*-butylnitramine was added to a solution of 4.0 g. of paraformaldehyde in 150 ml. of 82.5% sulfuric acid according to the conditions for compound I. The drowned reaction mixture precipitated 4.2 g. of product melting at 65–70°. This constitutes a 48% yield. Use of 74% sulfuric acid gave a 13% yield of the condensation product. One recrystallization from hexane gave the analytical sample melting at 72–73.5°.

Anal. Calcd. for $C_9H_{20}N_4O_4$: C, 43.54; H, 8.12; N, 22.57. Found: C, 43.32; H, 8.00; N, 22.44.

(B).—A mixture of 1.6 g. of *n*-butylnitramine, 50 ml. of dry ether, 1.0 g. of paraformaldehyde and 5 ml. of boron trifluoride etherate was refluxed for 8 hours, giving a clear solution. This was washed with 5 portions of water, dried with magnesium sulfate, and evaporated to give a small amount (*ca.* 0.2 g.) of a brown oil which, taken up in hexane and chilled, deposited a white solid, m.p. 72–73.5°, which gave no melting point depression when mixed with the material from method (A).

1,3-Dinitro-1,3-diazacyclopentane (IV). (A).—To a solution of 1.2 g. of paraformaldehyde in 50 ml. of 87% sulfuric acid was added 3.0 g. of EDNA according to the conditions for compound I. The drowned reaction mixture gave 1.8 g. of a white solid melting at 95–115°. This was added to 10 ml. of commercial 100% nitric acid chilled in an ice–salt bath, let stand 10 minutes, and poured onto ice to give 0.9 g. (28% yield) of a white solid melting at 128.5–133.5° (softening at 122°). Recrystallization from 50 ml. of 95% ethanol gave 0.6 g. of product melting at 132.5–134°.

(B).—To 58 ml. of 89% sulfuric acid, chilled in an ice–salt bath, was added 6.8 g. of N-methylol EDNA[3] over a period of 20 minutes. After 20 minutes of additional stirring the viscous mixture was poured onto an excess of ice to give 5.2 g. (85% yield) of product melting at 132.5–134°. This was recrystallized from 95% ethanol (50 ml./g.) to give an analytical sample melting at 132.5–133.5°.

Anal. Calcd. for $C_3H_6N_4O_4$: H, 3.73; N, 34.56. Found: H, 3.72, 3.92; N, 34.30, 34.49.

N-Methylol EDNA was recovered unchanged after being stirred for several hours at room temperature in trifluoroacetic anhydride containing a catalytic amount of boron trifluoride etherate.

Attempted Condensations with Other Primary N-Nitro Compounds.—The use of nitrourethan with solutions of paraformaldehyde in 80 to 90% sulfuric acid gave only water soluble products on drowning. Ether extraction of the aqueous solutions gave nitrourethan, identified by mixed melting point with the starting material.

The addition of cyclohexylnitramine to a solution of paraformaldehyde in 90% sulfuric acid gave a small amount of non-crystallizable yellow oil which could not be separated into recognizable products. The use of 75% sulfuric acid gave about 50% recovery of the starting nitramine and no other identifiable products.

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Esterification Catalysis by Metal Halides

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We have found that Friedel–Crafts type catalysts are very effective for accelerating the rate of reaction at low temperature between acid chlorides and polar alcohols, such as 2,2,2-trichloroethanol and 2,2,2-tribromoethanol. Anhydrous aluminum chloride is most active and ferric chloride, titanium tetrachloride, antimony pentachloride, boron fluoride, stannic chloride, zinc chloride and mercuric chloride are also useful in varying degree.

Examples of the catalytic effect of aluminum chloride are the preparations of β,β,β-trichloroethyl acetate and β,β,β-trichloroethyl 3,5-dinitrobenzoate. β,β,β-Trichloroethyl acetate has previously been prepared from acetyl chloride and trichloroethanol by methods requiring high temperature and long reaction periods.[1,2] The use of anhydrous aluminum chloride permits this reaction to occur easily in a solvent at low temperature.

At room temperature 1.56 g. (0.020 mole) of acetyl chloride and 3.00 g. (0.020 mole) of trichloroethanol were dissolved in 5 ml. of chloroform. Very little reaction was observed. The addition of 0.13 g. (0.001 mole) of crushed anhydrous aluminum chloride caused a vigorous exothermic reaction with copious evolution of hydrogen chloride gas. After five minutes 0.39 g. (0.003 mole) of additional aluminum chloride was added and the reaction continued vigorously for 10 minutes and then subsided. Warming to 45° completed the reaction in 20 minutes. The chloroform was evaporated and the residue treated with ice-cold dilute hydrochloric acid, extracted with ether, and distilled under vacuum after removal of the ether. A yield of 2.75 g.

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