Experimental

Preparation and Purification of Compounds.—*n*-Hexadecyl mercaptan purchased from the Connecticut Hard Rubber Company, m.p. 18°,[10b] was distilled at 0.6 mm., b.p. 135–140°. The middle cut was used for the spectrometric determination and for some of the other preparations described below. Analyses for carbon, hydrogen, and sulfur were satisfactory. ***n*-Hexadecyl sulfide** was prepared by the reaction of *n*-hexadecyl bromide[20] with sodium sulfide in alcohol; after recrystallization from 95% alcohol–hexane, colorless crystals, m.p. 58.2–58.5° (reported m.p. 57.5°[21]); analyses for carbon and hydrogen agreed with theory. ***n*-Hexadecyl disulfide** was prepared from *n*-hexadecyl mercaptan by oxidation with iodine in alcohol according to Collin *et al.*[10a]; recrystallization from acetone gave colorless needles, m.p. 55–55.5° (reported m.p. 54°[10a]). The sample for spectrometric analysis was recrystallized again from glacial acetic acid; analyses for carbon, hydrogen and sulfur agreed with the theoretical. ***n*-Hexadecyl trisulfide** was prepared from *n*-hexadecyl mercaptan and freshly redistilled sulfur dichloride according to the procedure of Clayton and Etzler[9]; recrystallization of the product from hexane–acetone gave colorless crystals, m.p. 42.0–42.6° (reported m.p. 41.2–41.9°[9]); analyses for carbon and hydrogen agreed with the theoretical. ***n*-Hexadecyl tetrasulfide** was prepared from *n*-hexadecyl mercaptan and sulfur monochloride according to the procedure of Clayton and Etzler[9]; recrystallization of the product three times from hexane–acetone gave a faintly yellow crystalline product, m.p. 36.8–37.2° (reported m.p. 35.9–36.5°[9]); analyses for carbon and hydrogen agreed with the theoretical. All preparations were repeated to verify the reproducibility of results. **Sulfur** (commercial, sublimed) was twice recrystallized from alcohol, m.p. 119° (capillary).

Determination of Ultraviolet Absorption Spectra.—The hexane used as a solvent in most of the determinations was purified by washing with 10% fuming sulfuric acid, followed by washing with aqueous sodium bicarbonate and water, then distillation through a Vigreux column. The spectrum of sulfur was determined in Commercial Solvents Gold Shield Absolute Alcohol as well as in hexane. Differences in the spectra in the two solvents were only observed at wave lengths below 230 mμ. Measurements were made in the Beckman Model DU Quartz Spectrophotometer in 1-cm. quartz cells. Values of log ϵ in the range 1–2 were measured at 10^{-2} M concentration, log ϵ 2–3 at 10^{-3} M, log ϵ 3–4 at 10^{-4} M, etc. Wave bands did not exceed 2.3 mμ. Most curves were checked on two different preparations of the same compound.

Mixed Melting Point Determinations.—It was of interest to determine whether mixtures of the various polysulfides would show depressions of melting point. For each of the several pairs of compounds, four simultaneous capillary melting point observations were made: specimens of each pure compound, a 2:1 mixture, and a 1:2 mixture of the two. The mixture of 1 disulfide: 2 trisulfide showed a 1°-depression below the m.p. of the pure trisulfide. The mixtures of the disulfide and tetrasulfide melted over wide ranges between the limits for the pure compounds. Mixtures of the trisulfide and tetrasulfide melted over ranges at intermediate values.

Acknowledgment.—Analyses of all compounds were made by Mrs. Sarah Miles Woods.

Summary

The ultraviolet absorption spectra of *n*-hexadecyl mercaptan, *n*-hexadecyl sulfide, *n*-hexadecyl disulfide, *n*-hexadecyl trisulfide, and *n*-hexadecyl tetrasulfide were determined in hexane solution. The spectra of sulfur in hexane and in ethanol solutions were determined. The spectra of the polysulfides have been shown to vary markedly with the sulfur content of the functional group. Spectrometry may be useful in the qualitative identification and quantitative estimation of various organic polysulfides.

PHILADELPHIA 4, PENNSYLVANIA
RECEIVED AUGUST 23, 1948

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(20) Purchased from Halogen Chemicals, Inc., Columbia, S. C.

(21) Fridau, *Ann.*, **83**, 16 (1852).

[CONTRIBUTION FROM THE FURMAN CHEMICAL LABORATORY, VANDERBILT UNIVERSITY]

The Synthesis of tris-(Hydroxymethyl)-methylnitramine and Other Compounds Related to tris-(Hydroxymethyl)-aminomethane[1]

BY JAMES CASON[2] AND FRANKLIN S. PROUT[2a]

In connection with studies on nitramines carried out in this country and Canada it became desirable to study the absorption spectra of an aliphatic nitramine and the isomeric nitrosohydroxylamine. The present communication describes the synthesis of such an isomeric pair. The study of the absorption spectra is reported separately by other authors.[3]

Although there have been prepared, in the aromatic series, nitramines isomeric with known nitrosohydroxylamines[4] there appears to be no report of the preparation and isolation in a pure condition of such an isomeric pair in the aliphatic series. In fact, there have been reported only a limited number of aliphatic nitrosohydroxylamines which are sufficiently stable to permit isolation in a pure state. tris-(Hydroxymethyl)-methylnitrosohydroxylamine has been prepared by Piloty and Ruff,[5] starting with tris-(hydroxymethyl)-nitromethane, and this preparation has been repeated by us with some modifications.

The method first investigated for the preparation of the previously unknown tris-(hydroxy-

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(1) This paper is based entirely on work done for the Office of Scientific Research and Development under Contract OEMsr-790 with Vanderbilt University.

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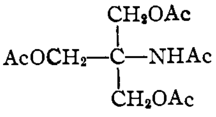
(3) Carmack and Leavitt, THIS JOURNAL, **71**, 1221 (1949).

(4) Hantzsch, *Ber.*, **31**, 177 (1898); **38**, 1000 (1905); Bamberger, *ibid.*, **27**, 363 (1894); **31**, 577 (1898); Bradfield and Orton, *J. Chem. Soc.*, 915 (1929); Marvel, "Org. Syn.," Coll. Vol. I, 177 (1941); Thiele, *Ann.*, **376**, 256 (1910); Neubauer, *ibid.*, **298**, 200 (1897).

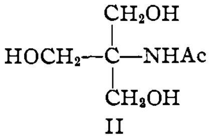
(5) Piloty and Ruff, *Ber.*, **30**, 1656 (1897).

methyl)-methylnitramine (VII) involved nitration of tetraacetyl tris-(hydroxymethyl)-aminomethane (I), but this route was unsuccessful for



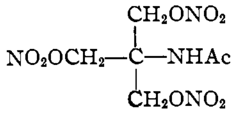
$$\mathrm{AcOCH_2{-}}\underset{\mathrm{CH_2OAc}}{\overset{\mathrm{CH_2OAc}}{\mathrm{C}}}\mathrm{{-}NHAc}$$

I



$$\mathrm{HOCH_2{-}}\underset{\mathrm{CH_2OH}}{\overset{\mathrm{CH_2OH}}{\mathrm{C}}}\mathrm{{-}NHAc}$$

II



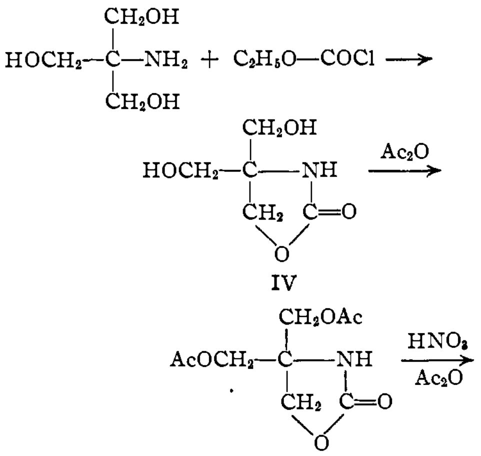
$$\mathrm{NO_2OCH_2{-}}\underset{\mathrm{CH_2ONO_2}}{\overset{\mathrm{CH_2ONO_2}}{\mathrm{C}}}\mathrm{{-}NHAc}$$

III

this amide resisted nitration by mixed acid, 98% nitric acid or nitric acid in acetic anhydride. The only product isolated from these attempted nitrations was starting material.

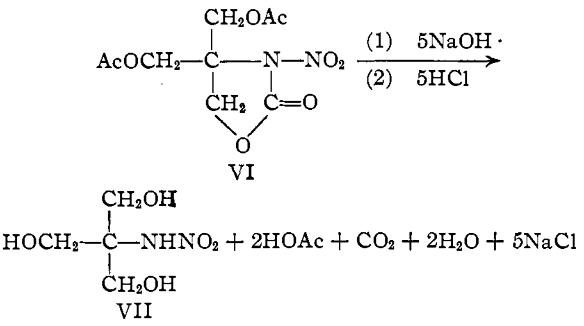
An attempt was also made to prepare the related tris-(nitroxymethyl)-methylnitramine, but it was found that nitration of N-acetyl-tris-(hydroxymethyl)-aminomethane (II) failed to affect the amide group; the only product isolated was N-acetyl-tris-(nitroxymethyl)-aminomethane. Two later attempts to obtain tris-(nitroxymethyl)-methylnitramine were also unsuccessful. The alkaline hydrolysis of 3-nitro-4,4-bis-(nitroxymethyl)-oxazolidone,[6] as well as nitration of tris-(hydroxymethyl)-methylnitramine failed to yield any isolable product.

A successful synthesis of tris-(hydroxymethyl)-methylnitramine (VII) was finally worked out, starting with 4,4-bis-(hydroxymethyl)-oxazolidone[6] (IV). The steps involved are outlined in the accompanying chart.



IV

V



VI

VII

Nitration of 4,4-bis-(acetoxymethyl)-oxazolidone (V) with a mixed acid containing excess sulfur trioxide resulted in nitrolysis of the acetyl groups to give 3-nitro-4,4-bis-(nitroxymethyl)-oxazolidone[6]; however, nitration with 98% nitric acid in acetic anhydride proceeded smoothly to give 3-nitro-4,4-bis-(acetoxymethyl)-oxazolidone (VI). Alkaline hydrolysis of the latter compound at room temperature gave a 77% yield of the desired tris-(hydroxymethyl)-methylnitramine (VII).

Experimental[7]

tris-(Hydroxymethyl)-methylhydroxylamine was obtained only after some modification of the method of Piloty and Ruff.[5] In the best procedure, a solution of 10 g. of tris-(hydroxymethyl)-nitromethane (recrystallized from nitromethane, m. p. 158–162°, with gassing) and 45 g. of crystalline aluminum sulfate in 300 cc. of water was stirred at 0–2° while 360 g. of 2.5% sodium amalgam was added during forty-five minutes. The mixture was stirred an additional forty-five minutes at the same temperature. After removal of aluminum hydroxide and mercury by filtration, the filtrate was concentrated to dryness *in vacuo* at a bath temperature of 50–60°. The residue was extracted at 100° with one 50-cc. portion and three 25-cc. portions of butanol. On standing overnight in the refrigerator, there crystallized from this extract 3.2 g. (35.2%) of heavy blades, m. p. 139–140°, with softening at 128°. On concentrating the butanol filtrate *in vacuo* a slightly waxy second crop weighing 0.4 g. was obtained. This hydroxylamine is not hygroscopic in moist air and it reduces Fehling solution instantly in the cold.

The product obtained as above contains a trace of sulfate, for its aqueous solution gives a slight cloudiness with barium hydroxide; however, this should be no disadvantage for use in preparation of the nitrosohydroxylamine. Piloty and Ruff[5] recommend removing sulfate by crystallization from alcohol containing "enough" barium hydroxide; however, in our hands, this procedure gave a product of lower melting point.

tris-(Hydroxymethyl)-methylnitrosohydroxylamine.[5]—A solution of 1.00 g. of the above-described hydroxylamine in 15 cc. of 0.484 *N* hydrochloric acid was cooled in an ice-salt-bath and treated with 0.504 g. of sodium nitrite in 4 cc. of water. The mixture was left in the cooling-bath for five minutes then the water was removed *in vacuo* at a bath temperature of 50–60°. The residue was dried *in vacuo* for one hour at this temperature then extracted at 50° with butanol (20, 10, 5 cc.). The extract was concentrated *in vacuo* at a bath temperature of 55–60°, then allowed to stand overnight in the refrigerator. There was obtained 0.66 g. (54.5%) of small, white dense crystals, m. p. 123–138° with continuous gassing.

The substance burns with a flash of brown fumes and does not reduce Fehling solution in the cold. It shows no evidence of decomposition on warming briefly in butanol or ethanol to 80°. Approximate solubilities at room tem-

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[6] 4,4-bis-(Hydroxymethyl)-oxazolidone and 3-nitro-4,4-bis-(nitroxymethyl)-oxazolidone were first prepared at Cornell University as a part of the investigation carried out under an OSRD contract and directed by Dr. A. T. Blomquist. The 3-nitro-4,4-bis-(nitroxymethyl)-oxazolidone was obtained by Blomquist by nitration of the oxazolidone, IV, with mixed acid, while nitration with 98% nitric acid gave the 4,4-bis-(nitroxymethyl) derivative. Publication of this work is planned for the near future (private communication, 11-18-48, from A. T. Blomquist).

[7] All melting points corrected.

perature are 2.5 g. per 100 cc. in ethanol and 0.6 g. per 100 cc. in butanol. It is very soluble in water, but not hygroscopic in moist air. The melting point behavior was unchanged by additional crystallization from butanol or ethanol. Since Piloty and Ruff[5] give the melting point as 147°, two samples were analyzed; sample NB-I-50B was recrystallized four times, sample NB-I-51 was recrystallized once.

Anal. Calcd. for $C_4H_{10}O_5N_2$: C, 28.92; H, 6.07. Found: (Sample NB-I-51) C, 29.05; H, 6.51; (Sample NB-I-50B) C, 29.21; H, 6.28.

Tetraacetyl tris-(Hydroxymethyl)-aminomethane[8] (I).—To a mixture of 415 cc. of acetic anhydride and 1 g. of sodium acetate was added 121 g. of commercial tris-(hydroxymethyl)-aminomethane (m. p. 146–161°). The amine went into solution rapidly, with evolution of heat, and the mixture soon refluxed so violently that external cooling was necessary. After spontaneous refluxing had ceased (longer heating is unnecessary) acetic acid was removed *in vacuo* and the residue was treated with Norit in benzene and crystallized at 0° from 700 cc. of benzene. The product so obtained was bulky and soft, and removal of benzene on the filter was exceedingly difficult; weight, 179.3 g., m. p. 97–107°. This product was crystallized from 200 cc. of acetic acid-400 cc. of ether, then from 125 cc. of acetic acid–300 cc. of ether; yield of soft white needles, 107.8 g., m. p. 114.0–114.5° (literature,[8] 115°). By systematically working up the mother liquors there was obtained an additional 57.5 g., m. p. 114.0–114.5°; total yield, 56%.

When this substance was prepared from pure tris-(hydroxymethyl)-aminomethane (m. p. 170.4–171.8°) the yield was not greatly improved, but pure material was obtained after one crystallization. Sodium acetate may be omitted if the reaction mixture is heated on a steam-bath for several hours.

N-Acetyl-tris-(hydroxymethyl)-aminomethane (II).—Tetraacetyl tris-(hydroxymethyl)-aminomethane (72.3 g.) was dissolved at room temperature in 800 cc. of 0.9844 *N* sodium hydroxide. After this mixture had remained at room temperature for three hours there was added an amount of standard hydrochloric acid equivalent to the alkali used. Water was removed *in vacuo* and the residue was extracted at 50° with 300 cc. of ethanol in four portions. After addition of 200 cc. of nitromethane, filtration of precipitated salt and concentration to 300 cc. there crystallized 11.5 g. of monoacetyl derivative, II, m. p. 131.3–133.4°. From the mother liquor was obtained 8.26 g. of product, m. p. 130–134°, total yield, 48.4%. This substance crystallizes with considerable difficulty. A sample crystallized from nitromethane for analysis melted at 133.6–134.0°.

Anal. Calcd. for $C_6H_{13}O_4N$: C, 44.16; H, 8.03. Found: C, 44.28; H, 8.13.

Attempts to prepare this compound in other ways were unsuccessful. When an aqueous solution of tris-(hydroxymethyl)-aminomethane was treated at room temperature with one mole equivalent of acetic anhydride, practically no crystalline monoacetyl derivative could be isolated from the reaction mixture. When a sample of tetraacetyl tris-(hydroxymethyl)-aminomethane was boiled with absolute ethanol containing a trace of anhydrous hydrogen chloride the starting material was essentially unaffected, and when the amount of hydrogen chloride was increased the material recovered was the hydrochloride of tris-(hydroxymethyl)-aminomethane, m. p. 150.0–150.8° (gas). Täuber[9] gives the melting point of this substance as "about 149°."

N-Acetyl-tris-(nitroxymethyl)-aminomethane (III).—A 4.08-g. sample of monoacetyl compound, II, was added during ten minutes, at 5–9°, to a mixture of 12.6 g. of 98% nitric acid and 12.8 g. of acetic anhydride. After the mixture had been stirred for four hours at 15–20° it was poured on 75 g. of cracked ice and the precipitate was collected and washed with water. The product was treated with sodium bicarbonate in 50 cc. of acetone and precipitated with 150 cc. of water. The oil which separated was seeded and the resulting crystallizate collected and dried; yield 6.26 g. (80.8%): m. p. 89.6–91.0°. This substance is crystallized with much difficulty. According to the best method discovered, 0.50 g. of nitrate was dissolved in 50 cc. of acetone and the solution diluted with 200 cc. of water. The recovery of slender needles was 0.16 g., m. p. 90.3–90.6°. The substance decomposes slowly at room temperature and rapidly at 56°; it was dried at 35° *in vacuo* for two hours for analysis. The analytical values show that only three nitro groups entered the molecule.

Anal. Calcd. for $C_6H_{10}O_{10}N_4$: C, 24.17; H, 3.38. Found: C, 24.69; H, 3.49.

Nitration of II with mixed acid gave water-soluble products at elevated temperatures and a poor yield of the trinitroxy compound at lower temperatures.

4,4-bis-(Hydroxymethyl)-oxazolidone (IV) was prepared by a slight modification of the procedure described by Blomquist.[6] To a solution of 121 g. of tris-(hydroxymethyl)-aminomethane (recrystallized, m. p. 167.6–170.6°) in 200 cc. of water was added, during two hours, at 5–10°, 124.8 g. (15% excess) of ethyl chlorocarbonate. During the last half of this addition there was added concurrently 46 g. of sodium hydroxide in 400 cc. of water. After addition was complete the cooling bath was removed and stirring continued for two hours, then solvent was removed as completely as possible *in vacuo* at a bath temperature of 55–65°. The residue was extracted with 550 cc. of absolute ethanol, and the residue obtained after removal of ethanol *in vacuo* was crystallized from methanol. Additional crops of product were obtained by addition of butanone and concentration. The total yield of IV was 100.3 g. (68%) distributed in five crops of melting point varying from 107.9–109.2° to 93–104°. One additional crystallization gave essentially pure material from low-melting crops; the best sample melted at 109.5–110.7°.

When only one equivalent of ethyl chlorocarbonate was used the yield was lower and there was difficulty in completely separating small amounts of the less-soluble starting material.

4,4-bis-(Acetoxymethyl)-oxazolidone (V).—A mixture of 29.4 g. of 4,4-bis-(hydroxymethyl)-oxazolidone (IV), 44.8 g. of acetic anhydride and 0.2 g. of sodium acetate was heated under reflux for five minutes, then concentrated to a sirup *in vacuo*. The mixture was seeded[10] and allowed to stand overnight, then ground under 50 cc. of ether. There was collected 39.4 g. (85.4%) of nearly colorless product melting at 57–68°. Three crystallizations from ethanol gave hard irregular plates melting at 69.0–70.4°.

Anal. Calcd. for $C_9H_{13}NO_6$: C, 46.75; H, 5.67. Found: C, 47.00; H, 5.66.

3-Nitro-4,4-bis-(acetoxymethyl)-oxazolidone (VI).—To a mixture of 16.6 g. of 98% nitric acid and 13.3 g. of acetic anhydride there was added during ten minutes, at 3–8°, 16.9 g. of 4,4-bis-(acetoxymethyl)-oxazolidone (V) as a sirup (crystalline material had not been obtained at that time). After stirring for two hours at 20–25° the homogeneous mixture was poured on 150 g. of cracked ice. The white precipitate, after collecting and drying, weighed 9.3 g., m. p. 89.4–90.8°. After three crystallizations from methanol there was obtained 7.11 g. of heavy elongated prisms melting at 97.1–97.8°.

Anal. Calcd. for $C_9H_{12}N_2O_8$: C, 39.14; H, 4.38. Found: C, 38.81; H, 4.63.

When V was nitrated with a mixed acid containing 5% excess sulfur trioxide the acetyls were nitrolyzed to some extent and the only product isolated was a slightly impure sample of **3-nitro-4,4-bis-(nitroxymethyl)-oxazolidone,**[6] m. p. 120.6–123.2°. A pure sample, prepared as de-

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(8) Piloty and Ruff, *Ber.*, **30**, 2066 (1897).

(9) Täuber, *Z. Krystallographie und Mineralogie*, **33**, 87.

(10) During early runs, persistent and varied efforts failed to induce crystallization of this substance; however, a sample which had stood for several weeks at room temperature was found crystalline.

scribed by Blomquist for comparison, melted at 124.3–124.9°. The mixed m. p. was 121–124°.

When 3-nitro-4,4-bis-(nitroxymethyl)-oxazolidone was hydrolyzed as described below in the preparation of tris-(hydroxymethyl)-methylnitramine, no product could be isolated from the reaction mixture.

tris-(Hydroxymethyl)-methylnitramine (VII).—A 4.42-g. sample of the nitro derivative, VI, was stirred mechanically with 116.5 cc. of 0.9844 *N* sodium hydroxide for two hours, mild cooling being used at first to prevent the temperature from rising above 35°. The solid dissolved after about one hour. The solution was treated with an amount of standard hydrochloric acid exactly equivalent to the sodium hydroxide used, then concentrated to dryness *in vacuo* (bath, 50–65°). The crystalline residue was extracted at about 50° with 125 cc. of butanol in three portions (extraction at 100° with nitromethane caused considerable decomposition). After filtration of salt the butanol solution was concentrated to dryness *in vacuo* (bath, 53–65°), leaving 2.84 g. of crude nitramine containing some salt, m. p. 114–117° (gas). One crystallization from nitromethane gave 2.04 g. (77%) of material melting at 123–125°. After two additional crystallizations from nitromethane very large striated blades and plates were obtained, m. p. 124–126° (gas), varying somewhat with rate of heating. The analytical sample, Code No. IV-20, was ground and dried *in vacuo* at 80°.

Anal. Calcd. for $C_4H_{10}N_2O_5$: C, 28.92: H, 6.07; mol. wt., 166.1. Found: C, 29.00; H, 6.26; mol. wt., 165.3 (by titration).

This nitramine is very soluble in water, moderately soluble in alcohol and essentially insoluble in acetone and ether. It shows no evidence of decomposition during crystallization.

When tris-(hydroxymethyl)-methylnitramine was nitrated at −5°, using a slight excess of 98% nitric acid in acetic anhydride, there was evolution of gas during the reaction, and the water-insoluble product which was obtained crystallized very slowly. Attempted recrystallization caused further decomposition, and no pure product could be obtained.

Summary

There has been prepared tris-(hydroxymethyl)-methylnitramine and the isomeric, previously known tris-(hydroxymethyl)-methylnitrosohydroxylamine. The preparation of several related compounds from tris-(hydroxymethyl)-aminomethane is also described.

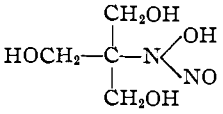
NASHVILLE, TENN. RECEIVED AUGUST 23, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Ultraviolet Absorption Spectra of tris-(Hydroxymethyl)-methylnitrosohydroxylamine, tris-(Hydroxymethyl)-methylnitramine, and their Salts[1,2]

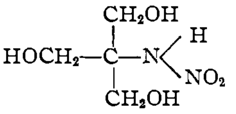
BY MARVIN CARMACK AND J. J. LEAVITT[3]

The synthesis by Cason and Prout[4] of tris-(hydroxymethyl)-methylnitrosohydroxylamine (I) and its isomer, tris-(hydroxymethyl)-methylnitramine (II), has afforded us the opportunity to investigate the ultraviolet absorption spectra of the primary nitramine and the isonitramine (nitrosohydroxylamine) chromophores in the rare, if not unique, situation in which both isomeric compounds are of the aliphatic series and isolable as reasonably stable crystalline compounds. In many of the more readily prepared nitrosohydroxylamine compounds, the presence of aromatic groups complicates the interpretation of the ultraviolet absorption spectra.



$(HOCH_2)_3C{-}N(OH){-}NO$

I



$(HOCH_2)_3C{-}N(H){-}NO_2$

II

As was hoped, ultraviolet spectrometry proved useful in studying the nature of the functional groups in certain nitramines or isonitramines of ambiguous structure which have been reported in the literature, as for example, "methylenebisisonitramine," prepared by the Traube reaction.[2,5,6]

Kortüm and Finckh[7] have published the ultraviolet absorption spectra of nitramide and methylnitramine in dilute hydrochloric acid and of dimethylnitramine in water. They also reported the spectra of hyponitrous acid in dilute hydrochloric acid, and of sodium hyponitrite, nitrohydroxylamine, and methylnitrosohydroxylamine in dilute sodium hydroxide. The alkylnitramines were measured only in neutral or acidic solution, while methylnitrosohydroxylamine was, unfortunately, measured only in alkaline solution; hence, the spectra of the two types of isomeric compounds are not directly comparable, and it is difficult from the data of Kortüm and Finckh to evaluate the suitability of spectrometry as a means of distinguishing one functional group from the other.

The spectrometric curves for tris-(hydroxyl-

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(1) This paper is based upon work carried out for the Office of Scientific Research and Development under Contract OEMsr-646, between the National Defense Research Committee and the University of Pennsylvania.

(2) R. Norman Jones and G. Denis Thorn have made a comprehensive study of the ultraviolet absorption spectra of nitramines and related compounds, including methylenebisisonitramine obtained by the Traube reaction. They will publish their results elsewhere (private communication).

(3) Present address: Calco Chemical Division, American Cyanamid Company, Bound Brook, N. J.

(4) Cason and Prout, THIS JOURNAL, **71**, 1218 (1949).

(5) Traube, *Ber.*, **27**, 1509, 3291 (1894); *cf.* also Wieland, *ibid.*, **61**, 2382 (1928).

(6) G. F. Wright and collaborators have studied the Traube product, methylenebisisonitramine, and will publish the results of their findings elsewhere (private communication).

(7) Kortüm and Finckh, *Z. physik. Chem.*, **48B**, 32 (1940).