left for 2 days at room temperature. The semicrystalline solid was warmed at 40–50°, the solid filtered and pressed between filter papers, washed with an ethanol–ether mixture, and dried. Crystallization by dissolving in ethanol and precipitating with ether gave 1.26 g. (79%) of slightly impure material. Further crystallizations gave purer material, m.p. 212–219° dec. The water-soluble acid gave postive ninhydrin and Millon's tests.

Anal. Calcd. for $C_{10}H_{10}F_3NO_3$: C, 48.19; H, 4.04; N, 5.62. Found: C, 48.10; H, 4.16; N, 5.49.

Infrared: 3600–3400 cm.$^{-1}$ (m, broad), —OH stretching; near 3100 cm.$^{-1}$ (s), —NH_3^+ stretching, part of broad band in 3200–2900-cm.$^{-1}$ region, including C—H stretching; twin bands at 1650 cm.$^{-1}$ (N) and 1615 cm.$^{-1}$ (vs), —COO^- stretching.

Ultraviolet spectra were measured in 95% ethanol (see discussion).

2-Amino-5-nitrobenzotrifluoride (VII).[2]—This compound was prepared in 97% yield by heating 2-chloro-5-nitrobenzotrifluoride with ammonia in a stainless steel bomb at 90° for 18 hr.

VII was heated with concentrated sulfuric acid to give yellow needles, m.p. *ca.* 270°, presumably 5-nitroanthranilic acid.[9] This material was treated with hot concentrated potassium hydroxide and the resulting solution acidified to give 5-nitrosalicylic acid, m.p. 234–235°. There was no depression on admixture with an authentic sample. VII gave the latter compound directly on reaction with alkali.

Attempted Synthesis of II from VII.—VII was treated with dilute sulfuric acid and potassium nitrite at 0° and the resulting solution slowly added to a boiling, saturated solution of copper sulfate under steam distillation conditions. The distillate was extracted with ether, the ethereal solution dried, and then evaporated to yield a brown oil. The oil was crystallized several times from ethanol–water mixtures to give a product melting at 95°, shown to be identical with starting material.

Nitration of *o*-Hydroxybenzotrifluoride.[10]—A. *o*-Hydroxybenzotrifluoride (5.0 g.) was placed in a 250-ml. Erlenmeyer flask and a solution containing 15 ml. of glacial acetic acid, 7.5 ml. of nitric acid, and 7.5 ml. water, was added while the flask was swirled in an ice bath. After the solid had dissolved, the flask was placed in the ice box overnight. No solid formed during this period, but a few small crystals adhered to the aluminum foil which covered the stopper. Several pieces of aluminum foil were added while the contents were swirled and the temperature allowed to rise. The contents of the flask darkened and after cooling overnight, there was obtained 2.6 g. of yellow crystals, m.p. 68–70°. Crystallization from an ethanol–water mixture yielded a product, m.p. 71.2–72.0° (cor.).

Anal. Calcd. for $C_7H_4F_3NO_3$; C, 40.59; H, 1.95; mol. wt., 207. Found: C, 40.25; H, 2.15; mol. wt., 216 (Rast).

Hydrolysis of this material with concentrated sulfuric acid gave a product, m.p. 146–148°, after crystallization from ethanol–water. Mixture melting point with authentic 3-nitrosalicylic acid showed no depression. The original product was, therefore, 2-hydroxy-3-nitrobenzotrifluoride.

B. VIII reacted with 8 *N* sulfuric acid and potassium nitrite to give, after work-up, yellow crystals of 2-hydroxy-3-nitrobenzotrifluoride, m.p. 69–71°.

Analyses were conducted by Micro-Tech Laboratories, Skokie, Ill., and by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Infrared spectra were measured with a Perkin–Elmer Model 21 double beam spectrophotometer using KBr pellets. Ultraviolet spectra were obtained on a Beckman DK-2 recording spectrophotometer.

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(10) Purchased from Pierce Chemical Co., Rockford, Ill.

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Aliphatic Nitrones

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Attempts to prepare aliphatic nitrones by the condensation of aliphatic aldehydes and N-alkylhydroxylamines, a reaction which yields C,C-disubstituted aliphatic nitrones from aliphatic ketones,[1] results only in the formation of dimers[2] or products from secondary reactions.[3] Alicyclic five-membered ring nitrones have been prepared either by reduction of γ-nitro ketones[4,5] or by oxidation of the corresponding hydroxylamine derivatives.[6] However, the parent six-membered ring nitrone has not been obtained by these methods since 1,3-dipolar addition takes place to form the dimer.[2] Recently we obtained N-methyl-C-4-hydroxytetramethylene nitrone from 5-hydroxypentanal *via* its cyclic N-hydroxylamino acetal.[7] To our knowledge this is the first synthesis of an aliphatic nitrone from the corresponding aldehyde.

Ruppert used hydrogen peroxide to oxidize aliphatic azomethines and obtained aliphatic nitrones,[8] which we have also succeeded in synthesizing by using the same reagent to oxidize O,N-cyclic acetals of 5-hydroxypentanal. These acetals are readily made by treating the cyclic hemiacetal of 5-hydroxypentanal with primary amines in the presence of potassium carbonate[9]; their infrared spectrum showed no absorption in the C=N region.

The N-alkyl-C-4-hydroxytetramethylene nitrones Ia and Ib obtained in this way could be distilled *in vacuo* without decomposition. Their infrared spectra on a sodium chloride plate showed a strong C=N absorption at 6.05 μ and a medium strong band at 6.4 μ which we attribute to the =N → O group, since in a polar solvent (chloroform) it shifted to 6.55 μ.[5]

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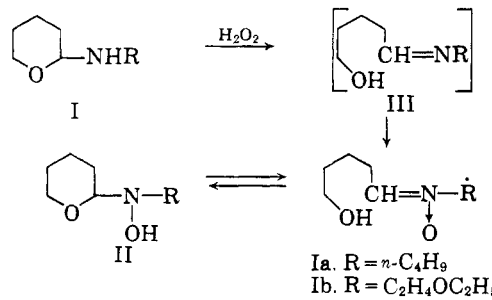

I III II

Ia. R = *n*-C_4H_9
Ib. R = $C_2H_4OC_2H_5$

We did not detect the presence of the tautomeric hydroxylamine derivatives II, although secondary amines are known to be oxidized preferentially to the N,N-disubstituted hydroxylamines.[10] Thus it appears that in the first step of this reaction the O,N-acetal was hydrolyzed to the corresponding azomethine III which was subsequently oxidized by the hydrogen peroxide to the nitrone I. The ready hydrolysis of O,N-acetals of 5-hydroxypentanal by water has been already reported by Glacet and Gaumeton.[9]

There is some indication that the nitrones I tautomerize to the tetrahydropyranylhydroxylamines II in alkaline solution. In 5% sodium hydroxide solution at room temperature the nitrone Ia gave an immediate positive hydroxylamine test with triphenyltetrazolium chloride[11] and reduced silver halide in the cold, whereas the N-*n*-propyl-C-ethylnitrone IV which was synthesized by Ruppert's method did not. The positive hydroxylamine test with triphenyltetrazolium chloride has to be judged with some caution since any nitrone is expected to be hydrolyzed to a N-alkylhydroxylamine in alkaline solution; however, it appears that this hydrolysis is not rapid at room temperature or else IV would also have caused the immediate reduction of silver halide.

Experimental[12]

N-*n*-Butyl-C-4-hydroxytetramethylene Nitrone (Ia).—Nine grams of 30% hydrogen peroxide was added dropwise with ice cooling to 11.5 g. of 2-*n*-butylaminotetrahydropyran.[9] After it had been stirred for 20 hr. at room temperature the reaction mixture was extracted with chloroform. By distillation of the dried chloroform extract was obtained 7.4 g. (58.5%) of N-*n*-butyl-C-4-hydroxytetramethylene nitrone, b.p. 151–152° (0.1 mm.); $n^{25}D$ 1.4712. $\lambda_{max}^{CHCl_3}$ (infrared) 2.95–3.03, 3.43, 6.03, 6.55, 6.82 μ.

Anal. Calcd. for $C_9H_{19}NO_2$: N, 8.09. Found: N, 8.28.

2-Ethoxyethylaminotetrahydropyran.—A 20.4-g. sample (0.2 mole) of 2-hydroxytetrahydropyran[13] was added dropwise with ice cooling to a stirred suspension of 13 g. of anhydrous potassium carbonate in 17.8 g. (0.2 mole) of ethoxyethylamine. The reaction mixture was stirred for 1 hr. at 0° and for 3 hr. at room temperature. It was then filtered and the insoluble potassium carbonate washed with ether. Distillation of the combined organic solutions gave 29 g. (84%) of 2-ethoxyethylaminotetrahydropyran, b.p. 69–70° (1.4 mm.); $n^{23}D$ 1.4502.

Anal. Calcd. for $C_9H_{19}NO_2$: 8.09. Found: N, 8.03.

N-Ethoxyethyl-C-4-hydroxytetramethylene Nitrone (Ib).—Ten grams of 35% hydrogen peroxide was added dropwise with stirring and ice cooling to 17.3 g. (0.1 mole) of 2-ethoxyethylaminotetrahydropyran. The mixture was stirred for 8 hr. at room temperature and extracted with chloroform. By distillation of the dried chloroform extract was obtained 8.2 g. (43.5%) of N-ethoxyethyl-C-4-hydroxymethylene nitrone, b.p. 168–172° (0.7 mm.); $n^{23}D$ 1.4695. $\lambda_{max}^{CHCl_3}$ (infrared) 2.92–3.02, 3.45, 6.02, 6.55, 6.87, 9.0 μ; (salt plate): 3.05, 3.4–3.5, 6.03, 6.4, 6.87, 8.95.

Anal. Calcd. for $C_9H_{19}NO_3$: C, 57.11; H, 10.12; N, 7.40. Found: C, 57.31; H, 10.25; N, 7.48.

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Oxidative Dimers of Benzaldehyde Phenylhydrazone

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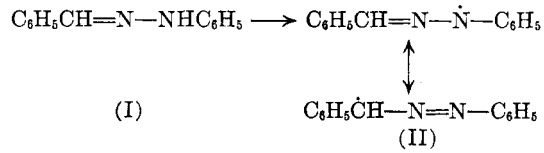
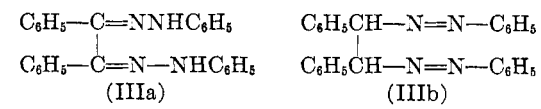
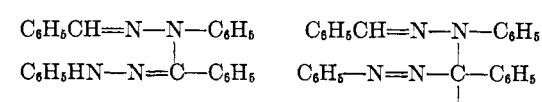
Benzaldehyde phenylhydrazone (I) has been oxidized with a variety of reagents including sodium ethoxide and iodine,[1] amyl nitrite,[2] mercuric oxide,[3] and oxygen.[4] The products have been characterized as substances of molecular formula $C_{26}H_{22}N_4$, there being considerable controversy as to the number and identity of the dimers formed. Coupling of the pseudo-allylic radical (II)



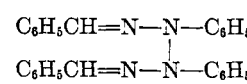
(I) (II)



(IIIa) (IIIb)



(IVa) (IVb)



(V)

in a C—C (IIIa), C—N (IVa) and N—N (V) manner has been proposed. The isomerization of the "N—N" dimer of m.p. 186° to benzil osazone

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