counts from 50-mg. pellets and 100-mg. pellets were the same.

It was attempted to determine the composition of the portion of the crude that was not copper phthalocyanine, phthalimide, and cyanuric acid, but without success. This portion of the crude was not identified by its infrared spectrum before or after extractions in water, ethyl alcohol, and α-chloronaphthalene in succession. Its small activity compared with the activity of the other portions of the reaction system indicates that it contained only a small amount of matter derived from the phthalic anhydride.

Four runs were made. Average weights of material and average activity of material with standard deviation are given in Table I. Also, average activity in terms of the C^{14}-phthalic anhydride is presented for each material; this value is calculated from the average weight of the material and the average activity of the material. The average activity in terms of the C^{14}-phthalic anhydride is comparable for all materials except for the portion of the crude that was not copper phthalocyanine, phthalimide, and cyanuric acid, indicating the presence of a small amount of matter derived from phthalic anhydride in this material.

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1-(N-Ethoxy)-1-ethylhydrazine

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In light of the current interest in organic derivatives of hydrazine and hydroxylamine we wish to report the preparation and characterization of the first reported N-alkoxyhydrazine. 1-(N-Ethoxy)-1-ethylhydrazine $[C_2H_5ON(C_2H_5)NH_2]$ was prepared by the reduction of N-nitrosodiethylhydroxylamine. Of several reducing agents tried, only lithium aluminum hydride gave the desired product.

This basic liquid reduced Fehlings solution, formed a crystalline acid oxalate, and condensed with *p*-nitrobenzaldehyde to give the hydrazone. The infrared and nuclear magnetic resonance spectra confirmed the nature of the new compound. Catalytic reduction of 1-(N-ethoxy)-1-ethylhydrazine acid oxalate in methanol with a platinum catalyst followed by addition of oxalic acid gave ethanol plus the oxalates of ammonia and ethylamine. This again pointed definitely to the correctness of the assigned formula for the new compound.

Experimental

Reduction of N-Nitrosodiethylhydroxylamine with Lithium Aluminum Hydride.—To 19.6 g. (0.17 mole) of N-nitrosodiethylhydroxylamine[1] in 200 ml. of dry diethyl ether at 3–5° was added dropwise, with stirring, a solution of 6.5 g. (0.17 mole) of $LiAlH_4$ in 200 ml. of diethyl ether. The mixture was stirred at room temperature for 3 hr. after the addition was completed, and the complex decomposed with 20 ml. of a 20% potassium sodium tartrate solution. The resulting solid was filtered and extracted continuously with diethyl ether for 50 hr. The combined ether extracts yielded, after drying and fractionation, 6.2 g. of a colorless liquid boiling at 80–81°. This liquid became light yellow on standing in the cold. The infrared spectrum differed considerably from the spectrum of O,N-diethylhydroxylamine, especially in the 10–12-μ region. Selected infrared maxima (NaCl plates) were 3.0, 3.4, 6.1, 9.6, and 11.5 μ. The nuclear magnetic resonance spectrum in $CdCl_2$ showed two triplets closely overlapped at τ 8.3 and two quartets closely overlapped at τ 5.9 in addition to a singlet at τ 7.0.

Anal. Calcd. for $C_4H_{12}N_2O$: C, 46.11; H, 11.63. Found: C, 45.96; H, 11.74.

1-(N-Ethoxy)-1-ethylhydrazonium Oxalate.—The acid oxalate was prepared by the addition of an ethereal solution of the hydrazine to a saturated solution of anhydrous oxalic acid in ether. The precipitated solid was washed with ether and recrystallized from absolute ethanol. The product was a white crystalline solid, m.p. 179–180°.

Anal. Calcd. for $C_6H_{14}N_2O_5$: C, 37.10; H, 7.28. Found: C, 37.31; H, 7.12.

Condensation of 1-(N-ethoxy)-1-ethylhydrazine with *p*-Nitrobenzaldehyde.—A few drops of 1-(N-ethoxy)-1-ethylhydrazine was added to a solution of *p*-nitrobenzaldehyde in methanol containing a drop of glacial acetic acid. Warming for a few minutes gave a yellow solid which, when recrystallized from dimethylformamide, had m.p. 307° dec.

Anal. Calcd. for $C_{11}H_{15}N_3O_3$: C, 55.67; H, 6.38. Found: C, 55.86; H, 6.09.

Reductive Cleavage of 1-(N-Ethoxy)-1-ethylhydrazonium Oxalate with Hydrogen–Platinum.—Crystalline 1-(N-ethoxy)-1-ethylhydrazonium oxalate (0.1 g.) was dissolved in 20 ml. of methanol, and 0.1 g. of brown platinum oxide was added. The mixture was placed in a Parr hydrogenator and shaken for 10 hr. at 50 p.s.i. The platinum was filtered and a small amount of the filtrate was tested for ethanol.[2] A positive test was obtained. The methanol used as solvent was tested in the same manner; it gave a negative test. To the remainder of the methanol solution was added 20 ml. of a saturated solution of anhydrous oxalic acid in ether. On the addition of 50 ml. of dry ether a precipitate formed; it was filtered. This solid was washed with ether and extracted with ethanol. The insoluble portion was found to be ammonium oxalate by infrared spectral comparison. To the ethanol-soluble portion dry ether was added and the precipitated solid was filtered. This solid was recrystallized from methanol–ether, m.p. 148–150°. A mixture melting point with known ethylammonium oxalate showed no depression (m.p. of mixture, 147–149°). The infrared spectrum of the known ethylammonium oxalate was identical with the spectrum of the ethanol-soluble oxalate.

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[1] A. B. Boese, Jr., L. W. Jones, and R. T. Major, *J. Am. Chem. Soc.*, **53**, 3530 (1931).

[2] F. Feigl, "Spot Tests in Organic Analysis," Elsevier Publishing Co., New York, N. Y., 1960, p. 358.

The Synthesis of 2,3,9,9a-Tetrahydro-6-hydroxy-5-methoxy-1-methyl-1*H*-benzo[*d,e*]quinolin-7(8*H*)-one

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As part of a program on the synthesis of analogs of the aporphine alkaloids[1] in which the D-ring is alicyclic, we have prepared 2,3,9,9a-tetrahydro-6-hydroxy-5-methoxy-1-methyl-1*H*-benzo[*d,e*]quinolin-7(8H)-one (**4**). This intermediate contains three rings of the aporphine nucleus and the features necessary for the attachment of the fourth ring by a route such as condensation with methyl vinyl ketone.

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[1] M. Shamma and W. Slusarchyk, *Chem. Rev.*, **64**, 59 (1964).