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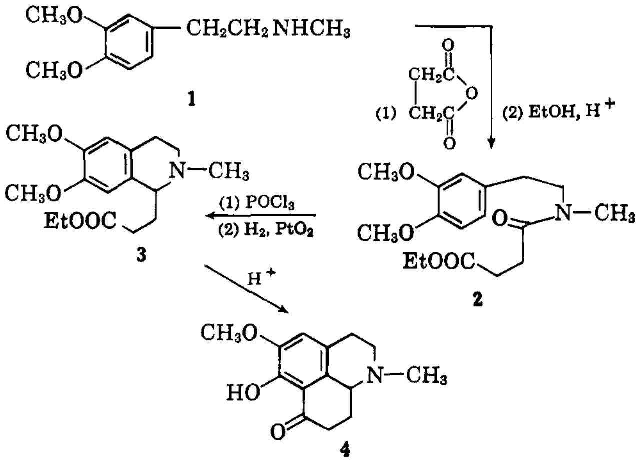
[1] M. Shamma and W. Slusarchyk, *Chem. Rev.*, **64**, 59 (1964).

Treatment of N-methyl-3,4-dimethoxyphenethylamine (1) with succinic anhydride followed by esterification gave the ester amide 2. This compound was also formed when the amine 1 was heated with diethyl succinate. Subjection of the ester amide 2 to the conditions of the Bischler–Napieralski[2] reaction gave a dihydro intermediate which after catalytic reduction afforded the tetrahydroisoquinoline 3. The polyphosphoric acid catalyzed cyclization of 3 gave the benzoquinolinone 4. The fact that demethylation had occurred in addition to cyclization was evidenced by the elemental analysis. (See Chart I.)

CHART I



The ether most likely to be cleaved is the one *ortho* to the ketone, since the aromatic ring joins the two in a vinylogous ester relationship. This proposal is verified by the infrared spectrum[3] of 4 which shows bands at 1632 (s) and 3000 (m, broad) cm.$^{-1}$. This is characteristic of an *o*-hydroxyketone chelate such as *o*-hydroxyacetophenone[4] which absorbs at 1638 (s) and 3000 (m, broad) cm.$^{-1}$, but not of *m*-hydroxyacetophenone[5] which shows a normal carbonyl band at 1680 (s) accompanied by free and associated hydroxy bands at 3600 (m, sharp) and 3300 (m, broad) cm.$^{-1}$.

The hydroxy group of 4 was not methylated by treatment with phenyltrimethylammonium hydroxide.[6] Since 4 did not readily undergo methylation, it was decided to discontinue this work.

Experimental[7]

Ethyl N-(3,4-Dimethoxyphenethyl)-N-methylsuccinamate (2). A. From Diethyl Succinate.—A mixture of 195 g. of 3,4-(dimethoxyphenethyl)-N-methylamine[8] and 1 kg. of diethyl succinate was heated at 200° for 4 hr. Distillation gave 156 g. (47%) of a colorless oil, b.p. 195° (0.25 mm.); $\lambda_{\max}^{\mathrm{EtOH}}$, m$\mu$ (ϵ), 229 (8900), 279 (2800).

Anal. Calcd. for $C_{17}H_{25}NO_5$: C, 63.14; H, 7.79; N, 4.34. Found: C, 63.04; H, 8.00; N, 4.33.

B. From Succinic Anhydride.—To a slurry of 50 g. of succinic anhydride in 100 ml. of benzene was added a solution of 97.5 g. of 3,4-dimethoxyphenethyl-N-methylamine in 100 ml. of benzene at a rate such that the temperature did not rise above 50°. Stirring was continued for 30 min., and then the solution refluxed for an additional 30 min. The reaction mixture was dissolved in 450 ml. of ethanol containing 3 ml. of sulfuric acid and refluxed for 2 hr. with partial removal of distillate. The ethanol was removed *in vacuo*, and the residue was poured into 200 ml. of ice–water. The mixture was made basic with sodium bicarbonate solution, saturated with sodium chloride, and extracted twice with 250-ml. portions of benzene. The benzene layers were combined, dried over sodium sulfate, and the solvent was removed. Distillation of the residue gave 127 g. (79%) of a colorless oil, b.p. 195° (0.25 mm.).

Ethyl 1,2,3,4-Tetrahydro-6,7-dimethoxy-2-methyl-1-isoquinolinepropionate (3).—To a refluxing solution of 50.4 g. of phosphorus oxychloride in 90 ml. of toluene was added, over a 30-min. interval, a solution of 97 g. of ethyl N-(3,4-dimethoxyphenethyl)-N-methylsuccinamate in 90 ml. of toluene. Refluxing was continued for an additional 75 min. The reaction mixture was poured into 600 ml. of ice–water, and the temperature was allowed to rise to 25° and held there until there was no exotherm upon removal of the cooling bath. The aqueous layer was made basic with 50% sodium hydroxide solution and extracted three times with 200-ml. portions of chloroform. The chloroform layers were combined and dried over sodium sulfate, and the solvent was removed. The residue was dissolved in 150 ml. of acetic acid, 500 mg. of platinum oxide was added, and the solution was hydrogenated at atmospheric pressure. Hydrogen uptake was constant after 0.20 (65%) equiv. of hydrogen had been absorbed. The catalyst was filtered and the solvent was removed *in vacuo*. Distillation of the residue gave 49 g. (53%) of a colorless oil, b.p. 172–185° (0.25 mm.). Redistillation gave an analytical sample, b.p. 170° (0.25 mm.); $\lambda_{\max}^{\mathrm{EtOH}}$, m$\mu$ (ϵ), 227 (8400), 279 (2600).

Anal. Calcd. for $C_{17}H_{25}NO_4$: C, 66.42; H, 8.20; N, 4.56. Found: C, 66.52; H, 8.33; N, 4.61.

The **hydrochloride** formed in ether and crystallized from ethanol as a white crystalline solid, m.p. 194–196°.

Anal. Calcd. for $C_{17}H_{26}ClNO_4$: C, 59.38; H, 7.62; Cl, 10.31; N, 4.07. Found: C, 59.57; H, 7.62; Cl, 10.45; N, 3.90.

2,3,9,9a-Tetrahydro-6-hydroxy-5-methoxy-1-methyl-1*H*-benzo[*d,e*]quinolin-7(8*H*)-one (4).—To 96 ml. of 85% phosphoric acid stirred in a nitrogen atmosphere was added 150 g. of phosphorus pentoxide, which resulted in an exotherm to 190°. The temperature was adjusted to 170° and 65 g. of ethyl 1,2,3,4-tetrahydro-6,7-dimethoxy-2-methyl-1-isoquinolinepropionate added over a 3-min. interval. The temperature was held at 170 to 180° for an additional 8 min. The reaction mixture was rapidly cooled to room temperature, 600 ml. of ice–water was added, and the temperature was held at 25° until complete solution was obtained. The solution was neutralized with 30% sodium hydroxide solution to pH 7.5 (approximate) and extracted with three 100-ml. portions of chloroform. The extracts were combined and dried over sodium sulfate, and the solvent was removed. Trituration of the residue with 70 ml. of petroleum ether (b.p. 30–60°) gave 21.0 g. (38%) of a solid, m.p. 94.5–97.5°. Recrystallization from Skelly solve B gave a light yellow crystalline solid, m.p. 105–105.5°; $\lambda_{\max}^{\mathrm{EtOH}}$, m$\mu$ (ϵ), 227 (16,000), 272 (8100), 364 (3560); $\lambda_{\max}^{1\,N\,\mathrm{NaOH}}$, m$\mu$ (ϵ), 239 (16,700), 279 (5400), 390 (5800).

Anal. Calcd. for $C_{14}H_{17}NO_3$: C, 67.99; H, 6.93; N, 5.66. Found: C, 68.00; H, 7.22; N, 5.86.

The **hydrochloride** formed in methanol and further recrystallization gave a white crystalline solid, m.p. 272°.

Anal. Calcd. for $C_{14}H_{18}ClNO_3$: C, 59.26; H, 6.39; Cl, 12.50; N, 4.94. Found: C, 59.01; H, 6.39; Cl, 12.39; N, 5.10.

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[2] For a review of this reaction see W. Whaley and T. Govindachari, *Org. Reactions*, **6**, 74 (1951).

[3] All spectra were measured on a Baird Model 4-55 double beam spectrophotometer equipped with sodium chloride optics. Dilute chloroform solutions were employed such that an increased dilution caused no further shift of the carbonyl absorption frequency. The materials used were obtained from Eastman Kodak.

[4] N. M. Cullinane, R. A. Woolhouse, and V. V. Bailey-Wood, *Rec. trav. chim.*, **80**, 116 (1961).

[5] H. H. Freedman, *J. Am. Chem. Soc.*, **82**, 2454 (1960).

[6] K. W. Bentley, "The Chemistry of the Morphine Alkaloids," Oxford, At the Clarendon Press, London, 1954, p. 60, and references therein.

[7] Melting points are uncorrected. The authors are indebted to Mr. R. Puchalski for the spectral data and Mrs. U. Zeek for analytical determinations.

[8] J. S. Buck, *J. Am. Chem. Soc.*, **52**, 4119 (1930).