monia by catalytic hydrogenation over palladium black.[7,8]

The isolated ammonia contained 0.80 atom % excess N^{15} while the aniline nitrogen contained only the natural abundance of N^{15}. On repetition of the experiment, the ammonia contained 1.25 ± 0.01 atom % excess N^{15} (expt. 2) and 1.13 ± 0.02 atom % excess N^{15} (expt. 3). The aniline in expt. 3 contained the natural abundance of N^{15}.

As a further check on these results a sample of the labeled sydnone was reduced with zinc and acetic acid to form N-phenylglycine and ammona.[11] When this ammonia was converted to nitrogen[12] and analyzed on the mass spectrometer, it was found to contain 1.30 ± 0.01 atom % excess N^{15} (expt. 2) and 1.19 ± 0.01 atom % excess N^{15} (expt. 3). It is therefore clear that rearrangement cannot occur to an extent greater than 1 or 2% and probably does not occur at all.[13]

The results of these experiments are thus consistent with the mechanism suggested for the acid hydrolysis of sydnones by Baker and Ollis.[3] They, of course, cannot be considered to prove this mechanism but, as is typical of tracer experiments, any alternative mechanism which may be suggested for this reaction must be consistent with the results reported here.

Experimental

N^{15}-Nitroso-N-phenylglycine.—N-phenylglycine (Eastman Organic Chemicals) was dissolved in 1 *N* hydrochloric acid (5 ml./g.), decolorized with charcoal, and precipitated by neutralization of the solution with 5 *N* sodium hydroxide. The precipitated N-phenylglycine was filtered, washed, and dried. The purified N-phenylglycine (5 mmoles) was dissolved in 25 ml. of 1 *N* hydrochloric acid and cooled to 0°. A solution of sodium nitrite (5 mmoles) containing 1% by weight of $KN^{15}O_2$ (Isomet Corp., assay 95.8% N^{15}) in 1 ml. of water was cooled to 0° and added slowly with stirring to the first solution. The oil which formed soon crystallized and was filtered, washed, and dried, m.p. 101–103°, lit.[2] m.p. 102–103°, 75% yield.

3-Phenylsydnone-2-N^{15}.—The above product was treated with acetic anhydride as described by Earl and Mackney,[2] m.p. 135–136°, lit.[2] m.p. 134–135°, 70% yield.

Acid Hydrolysis of 3-Phenylsydnone-2-N^{15}.—One millimole of the above sydnone was heated with 2 ml. of 5 *N* hydrochloric acid on a steam bath for 1 hr. On cooling, phenylhydrazine hydrochloride crystallized out, m.p. 230–235°, lit.[2] m.p. 233–234°, 84% yield.

Reduction of N^{15}-Labeled Phenylhydrazine.—The phenylhydrazine hydrochloride from the previous step was dissolved in 25 ml. of 50% aqueous ethanol and shaken with 0.1 g. of palladium black in an atmosphere of hydrogen at 1 atm. pressure until hydrogen uptake ceased (approximately 16 hr.). The reaction mixture was then acidified with hydrochloric acid, the catalyst was filtered off, and the filtrate was concentrated to a small volume. This sample was then made up to a known volume in a volumetric flask, and aliquots calculated to contain 1 to 2 μmoles of ammonia were taken for analysis by the Conway microdiffusion procedure.[15] Control samples of aniline and phenylhydrazine of similar concentration were analyzed in parallel. The ammonia titrations had to be corrected by subtracting 16% of the total volume of standard acid used in the titration; this allows for the aniline which diffused over in the time taken for quantitative diffusion of ammonia (2 hr.). There was no correction needed for any unreduced phenylhydrazine which may have been present. An aliquot of the hydrogenolysis mixture which contained 1 mg. of nitrogen was steam distilled into 10 ml. of 0.1 *N* sulfuric acid. This distillate which contains the ammonia from phenylhydrazine cleavage was concentrated to approximately 1 ml. and saved for analysis of its N^{15} content.

Isolation of Acetanilide.—Approximately one-half of the sample obtained after reduction of the labeled phenylhydrazine was evaporated to a small volume and treated with acetic anhydride and sodium acetate. Acetanilide was filtered and recrystallized, m.p. 111–113°, lit.[16a] m.p. 114°. Samples (10 to 15 mg.) of the isolated acetanilide were digested by the Kjeldahl procedure[16b] and the ammonia formed was distilled and titrated. This distillate was then evaporated to approximately 1 ml. and saved for mass spectrometric analysis of its N^{15} content.

N^{15} Analysis.—Ammonia samples were converted to nitrogen by use of sodium hypobromite as described by Rittenberg.[12] Aniline which was present in the ammonia samples did not interfere as no nitrogen is liberated when aniline is treated with the reagent. Unchanged phenylhydrazine would interfere, however, as it reacts with sodium hypobromite to liberate nitrogen quantitatively. On the other hand, this makes it possible to analyze phenylhydrazine directly for its N^{15} content when the position of the label does not have to be specified. Natural abundance was determined each day that a set of samples was analyzed, and standard samples of N^{15} ammonia were used for checking the accuracy of the analyses. These measurements were carried out on a Consolidated Electrodynamics Corp. mass spectrometer, Model 21-611.

Acknowledgment—We wish to thank Professor H. B. Waelsch of Columbia University for the loan of the mass spectrometer used in these studies.

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[7] H. Rupe and E. Hodel, *Helv. Chim. Acta*, **6**, 873 (1923).

[8] It has been established by the work of Holt and Bullock[9] and of Clusius and Hoch[10] that no N → N aryl migration occurs in this reaction. In addition, we prepared 1-phenylhydrazine-2-N^{15} and degraded it by this procedure to demonstrate that no rearrangement occurs under the identical conditions used to degrade the labeled phenylhydrazine obtained by hydrolysis of the labeled sydnone.

[9] P. F. Holt and B. I. Bullock, *J. Chem. Soc.*, 2310 (1950).

[10] K. Clusius and M. Hoch, *Helv. Chim. Acta*, **33**, 2122 (1950).

[11] J. C. Earl, *Rec. trav. chim.*, **75**, 346 (1956).

[12] D. Rittenberg, "Preparation and Measurement of Isotopic Tracers," Edwards, Ann Arbor, Mich., 1946, p. 31.

[13] A somewhat similar reaction in which migration of an aryl group from one nitrogen atom to an adjacent one seemed possible but was not observed is the Rowe rearrangement of a pseudophthalazone to a phthalazone.[14]

[14] W. R. Vaughan, D. I. McCane, and J. G. Sloan, *J. Am. Chem. Soc.*, **73**, 2298 (1951).

[15] E. J. Conway, "Microdiffusion Analysis and Volumetric Error," The MacMillan Co., New York, N. Y., 1958, p. 98.

[16] (a) Handbook of Chemistry and Physics, C. D. Hodgman, Ed., 44th Ed., The Chemical Rubber Publishing Co., Cleveland, Ohio, 1962, p. 768; (b) J. B. Niederl and V. Niederl, "Micromethods of Quantitative Organic Elementary Analysis," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1942, p. 69.

Formation of Copper Phthalocyanine

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Received January 7, 1964

The reaction mechanism of the formation of copper phthalocyanine in the phthalic anhydride–urea system remains to be determined. As a first step in the study of the mechanism of this reaction system it was determined that urea does not contribute its carbon to the phthalocyanine molecule in the formation of copper phthalocyanine.[1] As a second step in this study it is established that the α-carbon atom in the maleic anhydride ring in the phthalic anhydride remains in the reaction mass to form copper phthalocyanine, phthalimide, and a relatively small amount of compounds of as yet unknown composition. Phthalic anhydride containing α-C^{14}, *i.e.*, C^{14} in the C-7 position,

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[1] S. N. Brumfield, V. W. Foltz, C. M. McGhee, and A. L Thomas, *J. Org. Chem.*, **27**, 2266 (1962).

TABLE I

RUNS 1–4

Material	Weight, g. Initial	Weight, g. Final	Activity, c.p.m./mg.	Activity, c.p.m./mg. of C^{14}-phthalic anhydride
C^{14}-Phthalic anhydride	0.0012	...	...	...
Phthalic anhydride mix	5.00	...	12.6 ± 0.8	52,500
Reaction mixture	13.89	...	2.3 ± 0.1	26,600
Reaction crude	...	4.8 ± 0.5	11.4 ± 0.5	43,800
Copper phthalocyanine	...	3.5 ± 0.3	16.2 ± 0.3	62,000
Drierite	0	0.6 ± 0.6	0 ± 0	0
Ascarite–Drierite (tower)	0	4.8 ± 3.0	0 ± 0	0
Ascarite–Drierite (tube)	0	0.13 ± 0	0 ± 0	0
Activated charcoal	0	0	0 ± 0	0
Phthalimide condensate from reaction	...	0.5 ± 0.4	9.3 ± 2.7	38,800
Crude–copper phthalocyanine–phthalimide	...	1.0 ± 0.2	0.9 ± 0.2	6300 (max.)
Phthalimide condensate from sublimation	...	1.6 ± 0.4	8.1 ± 0.5	36,300

has now been used in the phthalic anhydride–urea reaction system. The copper phthalocyanine and phthalimide by-product made from this reaction system are radioactive. The carbon dioxide by-product is not radioactive although about 90% of the carbon in the urea is accounted for by weight in the form of carbon dioxide absorbed in Ascarite–Drierite. The remaining 10% of the carbon in the urea may be present as impurity in the form of ammonium carbonate and ammonium bicarbonate in recovered phthalimide (Table I).

Phthalimide is a familiar by-product and monoiminophthalimide[2] has been detected in the reaction mass from the phthalic anhydride–urea system. The presence of diiminophthalimide in the reaction mass has not been reported. Recently, in this laboratory, the presence of phthalonitrile has been detected in the reaction mass.

The fate of phthalic anhydride in this reaction system probably is phthalic anhydride → phthalimide → monoiminophthalimide → phthalocyanine and phthalic anhydride → monoiminophthalimide → phthalocyanine. The monoiminophthalimide may decompose rapidly to form phthalonitrile and water so that phthalonitrile, and not monoiminophthalimide, may be the immediate precursor of phthalocyanine.

The urea molecule is planar.[3] The angle between the two nitrogen atoms and the central carbon atom is 120°. The carbon atoms of phthalic acid are coplanar.[4] The distance between the nitrogen atoms in urea is 2.34 Å. The distance between the α-carbon atoms in phthalic acid is 2.98 Å. The urea molecule would make a "nice fit" into the embrace of the phthalic anhydride molecule to produce phthalonitrile, water, and carbon dioxide. If, on the other hand, the urea molecule and the phthalic anhydride molecule do not meet center-to-center, then the precursors of copper phthalocyanine may include not only phthalonitrile but also phthalimide, ammonia, and carbon dioxide as by-products. Phthalimide, carbon dioxide, ammonia, and water are major by-products.

Experimental

The reaction was carried out in a 300-ml. flask with a nitrogen carrier gas flow of about 1 ml./sec. through the reactor and downstream gas train consisting of two water condensers in series with cooling jacket maintained at 2° to trap sublimed phthalimide, a Drierite tube to trap water, a 50:50 Ascarite–Drierite tower to trap carbon dioxide, an Ascarite tube to test the efficiency of the Ascarite–Drierite tower, an activated charcoal tube to trap carbon monoxide, and a water bubbler.

The reaction mix (61.1 g.) was prepared from which four samples, each weighing 13.89 g., were drawn: 5.00 g. of phthalic anhydride mix, containing 1.2 mg. of carbon-14 phthalic anhydride of stated specific activity of 2.22 mc./mmole, 860 mg. of cuprous chloride, 20 mg. of molybdic trioxide, and 10 mg. of copper. The constituents were weighed on a Mettler balance with a stated sensitivity of about ±0.02 mg. The reaction mixture was ground and blended with mortar and pestle. The reaction mass was heated to temperature in 0.5 hr. and was held at 200° for 6 hr. The reaction product in the 300-ml. flask was weighed and copper phthalocyanine was determined colorimetrically at 430 mμ. It was ground in a mortar and pestle and was heated at 200° for 4 hr. in a 300-ml. flask with nitrogen purge into the flask. The nitrogen was vented to the atmosphere through a water condenser maintained at 2°. The condensate from this sublimation operation and the condensate from the reaction process were combined and weighed. The condensate was a mixture of phthalimide and ammonium carbonates. The residue in the reaction flask contained copper phthalocyanine and reaction by-products. The reaction by-products are soluble in dilute sulfuric acid and copper phthalocyanine is insoluble in dilute sulfuric acid. The residue was purified in 200 ml. of 10% sulfuric acid at 90° for 4 hr. The slurry was filtered over No. 1 Whatman paper and the residue was washed free of acid with about 500 ml. of distilled water. The residue was dried, weighed, and analyzed for copper phthalocyanine, which was in the range 94–98% by weight. To the combined filtrate of 10% sulfuric acid, wash water, and dissolved compounds, now at about pH 2, was added sodium hydroxide to pH 8, at which pH there was considerable flocculation. The slurry was cooled to 15° and was filtered over No. 1 Whatman paper. The residue was pale blue in color; it was dried and weighed. The pale blue residue contained cyanuric acid and sodium sulfate. Cyanuric acid and sodium sulfate were identified by their infrared spectra. The filtrate was evaporated to dryness. The infrared curve of the dry residue from the evaporated filtrate showed it to be sodium sulfate.

The C^{14} phthalic anhydride, phthalic anhydride mix, reaction mixture, reaction crude, phthalimide condensate, and purified copper phthalocyanine were radioactive. The contents of the Drierite tube, Ascarite–Drierite tower, and Ascarite–Drierite tube were weighed and ground. The contents of these three vessels, as well as the activated charcoal tube, gave no count. Determination of radioactivity was made by counting on 100-mg. samples of each of the above items with a Nuclear Corporation Model 2612-P portable radiation survey meter. A 100-mg. sample was placed into a 13-mm. KBr pellet die (Research and Industrial Instruments Co., MK-3). The assembled die was placed in a hydraulic press maintained at 10 mm. for 10 min. at about 120,000 lb./in.^{2}. Vacuum and pressure were removed from the die. The radioactive count was made on the pellet by placing the probe directly over and in contact with the pellet in the die. Background count was made in the same manner but without a pellet in the die. Radioactive count did not depend on the pellet thickness after a minimum thickness was obtained. Radioactive

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(2) G. Rosch, W. Wolf, and H. Vollman, U. S. Patent 2,727,043 (Dec. 13, 1955).

(3) J. E. Worsham, Jr., H. A. Levy, and S. W. Peterson, *Acta Cryst.*, **10**, 319 (1957).

(4) W. Nowacki, and H. Jaggi, *Z. Krist.*, **109**, 282 (1957).

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.

Acknowledgment.—The authors thank Dr. Frank H. Moser, Director of Research, and the Standard Ultramarine and Color Company for permission to publish these results. They thank Oscar L. Harvey, Jr., for his role in carrying out the experiments.

1-(N-Ethoxy)-1-ethylhydrazine

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Received December 17, 1963

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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Received December 30, 1963

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).