TABLE I

2,6-DIARYL-4-PYRONES FROM DIETHYL ACETONEDICARBOXYLATE

No.[a]	Phenol used	Yield, %	M.p., °C.	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found
I	Resorcinol	87	>300	$C_{17}H_{12}O_6$	65.38	64.97	3.87	4.02		
II	4-Chlororesorcinol	90	205–206.5	$C_{17}H_{10}Cl_2O_6$	53.56	54.01	2.64	2.88	18.60	18.29
III	Orcinol	46	>300	$C_{19}H_{16}O_6$	66.66	66.29	4.71	4.93		
IV	Phloroglucinol	100	176–177	$C_{17}H_{12}O_8$	59.30	58.97	3.51	3.82		
V	2,4-Dihydroxyacetophenone	48	149–149.5	$C_{21}H_{16}O_8$	63.63	63.39	4.06	3.89		
VI	2,4-Dihydroxybenzophenone	100	148–149.5	$C_{31}H_{20}O_8$	71.53	71.91	3.87	3.76		

[a] I, 2,6-bis(2,4-dihydroxyphenyl)-4-pyrone; II, 2,6-bis(2,4-dihydroxy-5-chlorophenyl)-4-pyrone; III, 2,6-bis(2,4-dihydroxy-6-methylphenyl)-4-pyrone; IV, 2,6-bis(2,4,6-trihydroxyphenyl)-4-pyrone; V, 2,6-bis(2,4-dihydroxy-5-acetylphenyl)-4-pyrone; VI, 2,6-bis(2,4-dihydroxy-5-benzoylphenyl)-4-pyrone.

TABLE II

p-Nitrobenzoate esters of I–VI series[a]					Spectral characteristics of I–VI series	
Compound used	Empirical formula	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found	Fluorescence, QRU[b]	Ultraviolet absorption bands in 200–350-mμ range (log ε)[c]
I	$C_{45}H_{24}N_4O_{18}$	161.5–163	6.16	5.98	5.93	284.2 (3.3), 327.0 (3.5)
II	$C_{45}H_{22}Cl_2N_4O_{18}$	174	5.73	5.57	69.20	263.7 (3.5), 332.5 (4.0)
III	$C_{47}H_{28}N_4O_{18}$	189–190.5	5.98	5.84	0.24	263.0 (3.7), 310.5 (4.03)
IV	$C_{59}H_{30}N_6O_{26}$	185–187	6.78	6.60	2.28	273 (3.7), 329 (3.9)
V	$C_{49}H_{28}N_4O_{20}$	159–161	5.64	5.82	0.02	282.5 (4.42), 317.5 (4.5)
VI	$C_{59}H_{32}N_4O_{20}$	175–176.5	5.01	5.20	0.01	264.8 (4.2), 295 (4.5), 329.5 (4.5)

[a] W. J. Hickinbottom, "Reactions of Organic Compounds," 3rd Ed., Longmans, Green and Co., New York, N. Y., 1957, p. 121. [b] QRU = quinine reference unit.[1] [c] Measurements made on a Bausch and Lomb Spectronic-505 in Spectro Grade methanol.

however, II was crystallized once from ethyl acetate, and IV was purified by first taking the compound up in ethyl acetate and precipitating the substance with heptane. The process was repeated for a second purification.

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Acid Hydrolysis of 3-Phenylsydnone-2-N^{15}

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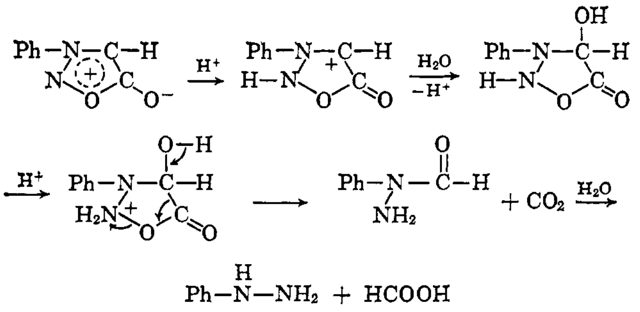
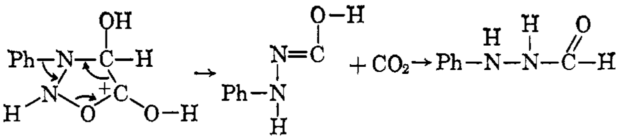
When N-phenylsydnone is hydrolyzed by acid, an internal oxidation-reduction reaction takes place with the formation of phenylhydrazine, formic acid, and carbon dioxide.[2] The mechanism shown below was suggested for this reaction by Baker and Ollis.[3] Aside from the nature of the end products of this hydrolysis, the strongest evidence cited by Baker and Ollis in support of their mechanism is the paper by Kenner and Mackay who reported the isolation of α-acylhydrazines when the hydrolysis was carried out in benzene with stoichiometric quantities of water and hydrochloric acid.[4] However, Kenner and Mackay gave no experimental evidence to support their conclusions and others have not been successful in repeating this work.[5]



In connection with attempts to prepare isosydnones,[6] the possibility of N → N aryl migration as a step in the acid hydrolysis of sydnones has been raised. This might be pictured as having the second protonation occur on the carbonyl oxygen and having the electron shift in the direction opposite to that postulated.[3]



This hypothesis could be tested readily by labeling one of the nitrogen atoms of the sydnone ring with N^{15} and determining the position of the label in the phenylhydrazine resulting from acid hydrolysis of the labeled sydnone.

This experiment was carried out by using N^{15}-labeled nitrite to prepare 3-phenylsydnone-2-N^{15}. After hydrolysis of the labeled sydnone, phenylhydrazine hydrochloride was isolated and degraded to aniline and am-

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(1) (a) Contribution No. 740 from the Chemistry Department, Fordham University, submitted by J. S. in partial fulfillment of the requirements for the M.S. degree. (b) A paper based on this work was presented at the 3rd Annual Metropolitan Regional Meeting of the New York Section of the American Chemical Society, Jan. 27, 1964.

(2) J. C. Earl and A. W. Mackney, *J. Chem. Soc.*, 899 (1935).

(3) W. Baker and W. D. Ollis, *Quart. Rev.* (London), **11**, 15 (1957).

(4) J. Kenner and K. Mackay, *Nature*, **160**, 465 (1947).

(5) I. M. Hunsberger, private communication.

(6) G. Sugerman, "Products Isolated in Unsuccessful Attempts to Prepare Isosydnones," Ph.D. Thesis, Chemistry Department, Fordham University, 1962.

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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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).