II in 100 ml. of tetrahydrofuran. Following 18 hr. of heating under reflux, the mixture was worked up in the same manner as above. The solid product was chromatographed over Florisil (elution with 5% acetone in ligroin) to afford 4.42 g. of crude IV followed by 1.68 g. of a higher melting compound. The former was recrystallized twice from cyclohexane to give 2.88 g. of the ketone IV, m.m.p. (with IV from VI) 146–148°.

The by-product IX was recrystallized from aqueous acetone to a constant melting point of 164–165°, ν_{max} 3375 and 1680 cm.$^{-1}$, λ_{max} 251 (ϵ 10,300) and 290 mμ (1280).

Anal. Calcd. for $C_{23}H_{30}O_3$: C, 80.21; H, 5.85. Found: C, 79.93, 80.63; H, 6.09, 6.21.

1-Methyl-3,4-dihydronaphthalene-3-carboxaldehyde, *p*-Toluenesulfonylhydrazone (VIII).—A solution of 17.84 g. of the acetal II in 400 ml. of tetrahydrofuran was added over 30 min. to an ice-cooled solution of 425 ml. of 2 *M* methylmagnesium bromide in benzene–tetrahydrofuran. Following 18 hr. of heating under reflux, the mixture was again cooled in ice and decomposed with 15 ml. of water followed by 250 ml. of saturated aqueous ammonium chloride. The organic layer was separated and washed with water and brine; the solvent was removed *in vacuo.* There remained 18.59 g. of viscous oil whose infrared spectrum shows no absorption in the carbonyl region.

A solution of 4.0 g. of VII, used as obtained above, and 10 ml. of 2.5 *N* hydrochloric acid in 100 ml. of acetone was stirred for 1 hr. at room temperature and then 1 hr. under reflux. The bulk of the solvent was removed on a rotary evaporator, the residue was dissolved in ether, and the solution was washed with water, sodium bicarbonate, and brine. The solvent was removed *in vacuo* to afford 2.80 g. of the crude aldehyde, ν_{max} 2750 and 1650 cm.$^{-1}$

The crude aldehyde in 50 ml. of ethanol was heated in the presence of 3.0 g. of *p*-toluenesulfonylhydrazine for 6 hr. The solution was allowed to cool and diluted with water. A gum came out which slowly solidified on scratching. This was recrystallized three times from methanol to afford 1.41 g. of the hydrazone VIII, m.p. 156–158° dec.

Anal. Calcd. for $C_{19}H_{20}N_2O_2S$: C, 67.04; H, 5.92; N, 8.23. Found: C, 66.62; H, 6.18; N, 8.28.

2-Di(*p*-methoxyphenyl)methyl-1-tetralone (V).—A solution of 10.0 g. of the acetal II in 200 ml. of tetrahydrofuran was added to an ice-cooled solution of the Grignard reagent prepared from 27.6 g. of *p*-bromoanisole and 5.6 g. of magnesium in 300 ml. of tetrahydrofuran. The reaction was run and the reaction mixture was worked up as above. The crude product was chromatographed over Florisil (elution with 3% acetone in ligroin); the combined crystalline fractions were recrystallized from ligroin to afford 11.13 g. of V, m.p. 105–108°.

A small sample was recrystallized from acetone–ligroin to give V, m.p. 103.5–105°; n.m.r., 12 protons above δ 6.5, doublet at 4.6, singlet 3.75, multiplets at 3.38, 2.95, and 2.0.

Anal. Calcd. for $C_{25}H_{24}O_3$: C, 80.62; H, 6.50. Found: C, 80.09; H, 6.60.

Reaction of 2-Di(*p*-methoxyphenyl)methyl-1-tetralone with Hydrobromic Acid.—A mixture of 2.0 g. of the ketone V and 60 ml. each of 48% aqueous hydrobromic acid and acetic acid was heated overnight at reflux. The volume was reduced to 70 ml. *in vacuo* and then the mixture was diluted with water and extracted with ether. The extracts were washed with aqueous sodium bicarbonate and brine and taken to dryness. The residual oil was chromatographed over Florisil (elution with 3% acetone in ligroin) to afford 0.37 g. (47%) of an oil whose infrared spectrum is identical with that of α-tetralone. The 2,4-dinitrophenylhydrazone of the oil melted at 258° dec., m.m.p. (with authentic α-tetralone 2,4-dinitrophenylhydrazone) 259° dec.

Reaction of 2-Diphenylmethyl-1-tetralone with Hydrobromic Acid.—Two grams of the ketone was treated exactly as above in 60 ml. each of 48% hydrobromic acid and acetic acid. The mixture was diluted with water and extracted with methylene chloride-ether. The oily solid which remained when the extracts were taken to dryness was crystallized twice from cyclohexane to afford 1.06 g. of the ketone, m.p. 141–144°.

Acknowledgment.—The author is indebted to Dr. Philip F. Beal, III, of these laboratories for valuable discussions concerning the n.m.r. spectra of these compounds.

A Synthesis of Polyhydroxy-2,6-diaryl-4-pyrones

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In a previous contribution[1] we have shown that when diethyl acetonedicarboxylate reacts with certain phenols in the presence of trifluoroacetic acid in a mole to mole ratio, ethyl coumarinacetates are formed. However, when the mole ratio is changed to two of the phenol to one of the ester, a polyhydroxy-2,6-diaryl-4-pyrone is produced as shown in the formula below. This reaction provides a one-step general process for the preparation of hydroxydiarylpyrones in acid media, a possibility not available by the method of Soliman and Kholy[2] or other earlier procedures.[3]

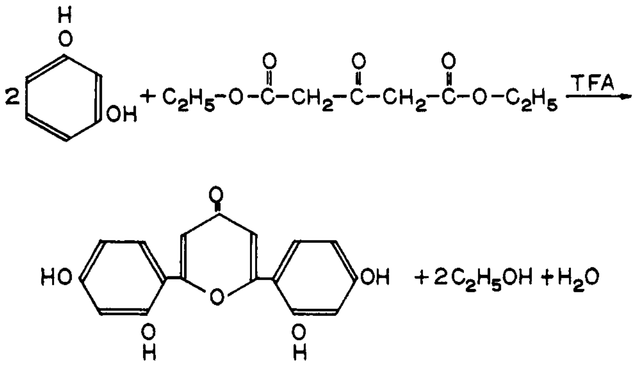

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Table I lists the compounds synthesized along with some pertinent physical data. Table II gives the *p*-nitrobenzoate esters of the members of the series and enumerates some of the spectral characteristics of the compounds. The fluorescence of some of the members of the series is of particular interest because three of them, compounds I, II, and IV, are much more fluorescent than quinine sulfate.

Compound I was selected as a model of the series to be subjected to alkaline degradation as proof of the proposed structures. Degradation in 30% potassium hydroxide[4] produced 2,4-dihydroxybenzoic acid, m.p. 208–210° dec., identical with an authentic sample.

Experimental[5]

Preparation of Members of I–VI Series.—A mixture consisting of 0.2 mole of the phenol, 0.1 mole of diethyl acetonedicarboxylate, and 30 ml. of trifluoroacetic acid was refluxed in the hood for 18 hr. The resulting solutions were diluted with about 150 ml. of water and chilled. The precipitates were filtered and dried in air. The analytical samples were obtained in most cases by recrystallizing the crude compound twice from boiling heptane;

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[1] L. L. Woods and J. Sapp, *J. Chem. Eng. Data*, **8**, 235 (1963).

[2] G. Soliman and I. E. Kholy, *J. Chem. Soc.*, 1755 (1954).

[3] R. C. Elderfield, "Heterocyclic Compounds," Vol. 1, John Wiley and Sons, New York, N. Y., 1952, p. 370.

[4] T. A. Geissman, "The Chemistry of Flavonoid Compounds," Macmillan and Co., New York, N. Y., 1962.

[5] Analyses were performed by Dr. Carl Tiedcke, Teaneck, N. J. All melting points were taken on a Fisher-Johns melting point block.

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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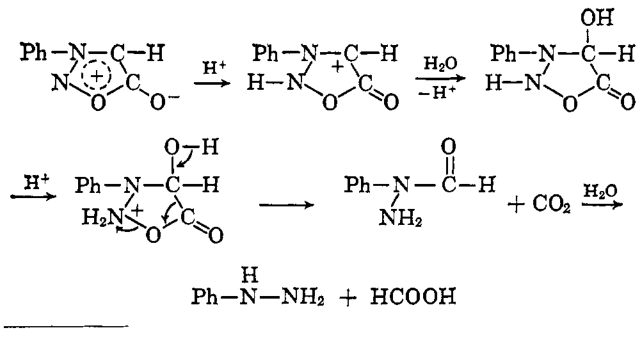
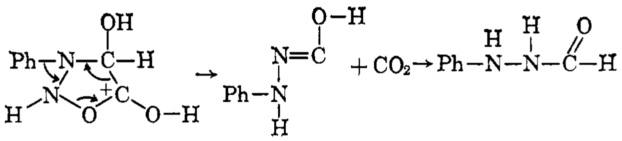
When N-phenylsydnone is hydrolyzed by acid, an internal oxidation-reduction reaction takes place with the formation of phenylhydrazine, formic acid, and carbon dioxide.[2] The mechanism shown below was suggested for this reaction by Baker and Ollis.[3] Aside from the nature of the end products of this 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.