Anal. Calcd. for $C_{17}H_{12}Cl_6O_6$: C, 38.89; H, 2.30; Cl, 40.52. Found: C, 39.06, 39.02; H, 2.35, 2.10; Cl, 40.20.

C. *Ethers.* The diethers of enol isomers V and VI were prepared by treating the enol isomer in acetone solution with ethyl bromide and potassium carbonate according to the method described in Hickinbottom.[18]

Diethyl ether of enol isomer V. M.p. 153–154°; conversion 85%.

Anal. Calcd. for $C_{17}H_{18}Cl_4O_4$: C, 47.96; H, 4.23; Cl, 33.12. Found: C, 47.87, 47.84; H, 4.32, 4.41; Cl, 32.54, 33.18.

Diethyl ether of enol isomer VI. M.p. 99–101°.

Anal. Calcd. for $C_{17}H_{17}Cl_5O_4$: C, 44.14; H, 3.70; Cl, 38.32. Found: C, 44.29, 44.02; H, 3.72, 4.13; Cl, 38.17.

Preparation of 5,6,7,8-tetrachloro-9,9-dimethoxy-2,3,4a,5,8,-8a-hexahydro-5,8-methanonaphthalene-1,4-dione. VIII. A. *From adduct* II. A solution containing adduct II (5 g.; 0.013 mole), methanol (200 ml.), stannous chloride dihydrate (30 g.; 0.13 mole), and hydrochloric acid (40 ml.) was shaken until the color disappeared. Water was added and the white solid which formed was recrystallized from methanol to give VIII (4.9 g.; 98%), m.p. 128–129°.

Anal. Calcd. for $C_{13}H_{12}Cl_4O_4$: C, 41.74; H, 3.23; Cl, 37.92. Found: C, 42.38, 41.91; H, 3.15, 2.87; Cl, 38.28.

B. *From adduct* III. A solution of adduct III (5 g.; 0.012 mole), iron (by reduction) (15 g.; 0.27 mole), and acetic acid (100 ml.) was refluxed for 1.5 hr. The solution was filtered while hot, and water was added to precipitate the product. The mixture was allowed to stand overnight before it was filtered and the product which was obtained was recrystallized twice from methanol-water to give VIII in 80% conversion; m.p. 129–131.°

Anal. Calcd. for $C_{13}H_{12}Cl_4O_4$: C, 41.74; H, 3.23; Cl, 37.92. Found: C, 42.23, 42.20; H, 3.61, 3.64; Cl, 37.82.

C. *From adduct* IV. Compound VIII was prepared from adduct IV in a manner similar to that described for the preparation from adduct III. It was obtained in 72% conversion, m.p. 129–132°.

Anal. Calcd. for $C_{13}H_{12}Cl_4O_4$: C, 41.74, H, 3.23; Cl, 37.92. Found: C, 41.18, 41.89; H, 3.31, 2.97; Cl, 37.82.

Preparation of the bis-2,4-dinitrophenylhydrazone of VIII. An excess of specially prepared[19] 2,4-dinitrophenylhydrazine reagent was added to a solution of VIII in ethanol (25 ml.). The bright yellow precipitate was filtered and washed with water. It was then recrystallized once from xylene, twice from acetic acid, and once more from xylene to give the bright yellow derivative in 30% conversion. Decomposition temperature, 234°.

Anal. Calcd. for $C_{25}H_{20}Cl_4N_8O_{10}$: Cl, 19.31; Found, Cl, 19.27.

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[18] W. J. Hickinbottom, *Reactions of Organic Compounds*, 2nd Ed., Longmans, Green and Co., London, 1948, p. 92.

[19] G. D. Johnson, *J. Am. Chem. Soc.*, **73**, 5888 (1951).

Condensation Reactions of Phthalaldehydic Acid. II

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Many of the reactions of phthalaldehydic acid can best be accounted for by using the tautomeric closed-ring structure. That such a structure actually exists has been verified recently through infrared absorption studies.[1] A previous paper by this writer[2] reported a number of condensation reactions of phthalaldehydic acid with aromatic hydrocarbons and with aryl halides which involve the reactive 3- position in the 3-hydroxy form of the acid.[3] Sulfuric acid in various concentrations was employed as the condensing agent. In all of the substituted phthalides which were synthesized in this manner, the carbon at the 3- position became linked directly to carbon in the aromatic ring.

The investigations reported in this paper show that this same general method can be used for condensing phthalaldehydic acid with phenols, phenolic ethers, and ring halogenated phenols and phenolic ethers. Bistrzycki[4,5] and his associates have reported success in preparing 3-(*p*-methoxyphenyl)phthalide by this approach, but they failed in attempts to similarly synthesize 3-(*p*-ethoxyphenyl)phthalide. In a series of papers Adams,[6] *et al.* describe condensations of opianic acid with a number of phenolic compounds, and suggest a similar behavior for phthalaldehydic acid.

The structures of certain phthalides which are formed in condensations of this type can be established with reasonable certainty on the basis of the relative directive strengths of the substituent groups. Thus, the condensation product to be expected from the reaction of phthalaldehydic acid with *p*-chloroanisole is 3-(5-chloro-2-methoxyphenyl)phthalide, and not the isomeric 3-(2-chloro-5-methoxyphenyl)phthalide. That this is a correct conclusion was proved unequivocally by converting this phthalide into 5-chloro-2-methoxyaniline and *o*-phthalic acid. To this end the phthalide was first oxidized with alkaline permanganate to produce the corresponding substituted *o*-benzoylbenzoic acid. From this compound there was prepared the oxime, isolated as an oxime anhydride. Heating the oxime with concentrated hydrochloric acid brought about a Beckmann rearrangement, and subsequent hydrolysis. Two products were isolated from the reaction mixture and identified as 5-chloro-2-methoxyaniline and *o*-phthalic acid.

Infrared absorption spectra were obtained for 3-phenylphthalide, a compound previously reported,[2] and also for 3-(5-chloro-2-methoxyphenyl)-phthalide and 3-(5-methyl-2-methoxyphenyl)-

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[1] D. D. Wheeler, D. C. Young, and D. S. Erley, *J. Org. Chem.*, **22**, 556 (1957).

[2] Part I appeared in *J. Org. Chem.*, **25**, 643 (1960).

[3] It is to be noted that prior to 1937 *Chemical Abstracts* used the notation 2-substituted phthalides instead of 3-substituted phthalides.

[4] A. Bistrzycki and G. Oehlert, *Ber.*, **27**, 2632 (1894).

[5] A. Bistrzycki and S. Zen-Ruffinen, *Helv. Chim. Acta*, **3**, 369 (1920).

[6] M. M. Brubaker and R. Adams, *J. Am. Chem. Soc.*, **49**, 2279 (1927).

phthalide. These spectra show intense absorption at 5.73 μ, 5.68 μ, and 5.70 μ respectively, attributed to C═O stretch as affected by five-membered ring strain. Intense bands also occur at 9.33 μ, 9.48 μ, and 9.40 μ, respectively, and are assigned to asymmetric C—O—C stretch. For 3-phenylphthalide and 3-(5-methyl-2-methoxyphenyl)phthalide strong absorption occurs at 10.35 μ and 10.25 μ, respectively, due to symmetric C—O—C stretch. No pronounced absorption is evident in this region for 3-(5-chloro-2-methoxyphenyl)phthalide; the symmetric C—O—C stretch is particularly sensitive to the group attached at the 3- position. Wheeler, Young, and Erley[1] have noted these same three absorption bands for a number of 3-substituted phthalides in which the carbon at this position is linked to an element other than carbon. Their suggestion that these bands have value in the identification of phthalide derivatives is strengthened by the infrared data cited here

With the exception of 3-(*p*-methoxyphenyl)-phthalide, the phthalides whose syntheses are reported here are believed to be new compounds.

EXPERIMENTAL

The phthalaldehydic acid used in this study was supplied by the Dow Chemical Co.; it was purified as previously described.[2] The ratios of acid to water, and of acid to acid, are on a volume basis.

3-(p-Methoxyphenyl)phthalide. One and one-half grams (0.01 mole) of phthaladehydic acid was dissolved in 24 ml. of 3:1 concd. sulfuric acid–water. This solution was cooled in an ice water bath and 1.08 g. (0.01 mole) of anisole was added. The cold mixture was mechanically stirred to disperse the anisole. After about 1 hr. the mixture became light red in color and homogeneous. Stirring was continued for an additional 0.5 hr. to insure complete reaction. Upon pouring the reaction mixture into about ten times its volume of cold water a soft, yellow solid separated; this soon became sufficiently hard to crumble. Thorough washing and air-drying gave 2.4 g. (100%) of crude product. This was recrystallized from glacial acetic acid, and washed on the filter with a small volume of ice-cold ethanol. The nearly white crystalline product melted at 116–117° and weighed 1.85 g. (77%), lit.[7] m.p. 116–117°.

Anal.[8] Calcd. for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 75.14; H, 5.23.

3-(p-Ethoxyphenyl)phthalide. One and one-half grams (0.01 mole) of phthalaldehydic acid was dissolved in 18 ml. of 2:1 concd. sulfuric acid–water, and the solution cooled in an ice water bath. To this was added 1.22 g. (0.01 mole) of phenetole, and the cold mixture was then mechanically stirred. After 2 hr. soft, white, bead-like curds separated. The mixture was kept cold and stirred for an additional 3 hr. The crude product was isolated as described for 3-(*p*-methoxyphenyl)phthalide; it weighed 2.2 g. (87%). Recrystallization from ethanol gave 1.7 g. (67%) of white crystals, m.p. 110–111°.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.69; H, 5.42.

3-(5-Chloro-2-methoxyphenyl)phthalide. The reaction mixture was prepared by dissolving 1.5 g. (0.01 mole) of phthalaldehydic acid in 25 ml. of 4:1 concd. sulfuric acid–water, then adding 1.42 g. (0.01 mole) of *p*-chloroanisole. This was stirred mechanically at room temperature for a period of 6 hr., and then poured into a large volume of cold water. The crude phthalide separated at once as a pale yellow solid. Crushing, washing with cold water, and air-drying gave 2.52 g. (92%) of crude product. Recrystallization from ethanol yielded 1.95 g. (71%) of white needle-like crystals, m.p. 126–127°.

Anal. Calcd. for $C_{15}H_{11}O_3Cl$: C, 65.58; H, 4.04; Cl, 12.91. Found: C, 65.88; H, 3.92; Cl, 13.03.

o-Phthalic acid and 5-chloro-2-methoxyaniline from 3-(5-chloro-2-methoxyphenyl)phthalide. That the condensation of phthalaldehydic acid with *p*-chloroanisole, which conceivably could lead to the formation of one or both of two possible isomers, gave 3-(5-chloro-2-methoxyphenyl)phthalide as the only isolated product was proved as follows. One gram of this phthalide was oxidized by use of alkaline permanganate solution in the usual manner. The crude oxidation product was recrystallized from aqueous ethanol; this gave 0.87 g. of a white solid, m.p. 141–141.5°. Neut. equiv. Calcd. for $C_{14}H_{10}O_2Cl \cdot COOH$: 290.7. Found: 291.2.

The oxidation product was converted into the corresponding oxime anhydride by following essentially a procedure outlined by Thorpe.[9] Recrystallization of the crude oxime anhydride from ethanol gave 0.7 g. of white fibrous needles, m.p. 174–175°. A successful Beckmann rearrangement, followed by hydrolytic splitting, was carried out by suspending 0.2 g. of the oxime anhydride in 10 ml. of concd. hydrochloric acid. This mixture was sealed in a glass tube and heated for a total of 6 hr. in an oil bath maintained at 125–130°; during this time the suspended solid gradually disappeared. After standing undisturbed for 24 hr. a crystalline solid separated upon shaking the tube. This proved to be *o*-phthalic acid. Following removal of the *o*-phthalic acid the solution was carefully neutralized with sodium hydroxide solution. Fine glistening plates, somewhat dark in color, separated. Recrystallization from aqueous ethanol gave plates of pronounced aniline-like odor, m.p. 82–83°. The accepted melting point for 5-chloro-2-methoxyaniline is 82–83.5.° A mixed melting point with an authentic sample showed no depression. A small quantity of the picrate of this compound was prepared; it gave a melting point of 194–195°; lit. m.p. 194°.

3-(5-Chloro-2-ethoxyphenyl)phthalide. One and one-half grams (0.01 mole) of phthalaldehydic acid was dissolved in 25 ml. of 4:1 concd. sulfuric acid–water solution. To this was added 1.57 g. (0.01 mole) of *p*-chlorophenetole, and the mixture then mechanically stirred at room temperature to disperse the *p*-chlorophenetole. After a period of 6 hr. the mixture was milky with fine particles of solid in evidence. This was then poured into about ten times its volume of cold water; granules of pink solid separated at once. The 2.47 g. (85%) of crude product, when recrystallized from glacial acetic acid, afforded 2.1 g. (73%) of a granular, crystalline, white solid. An analytical sample melted at 164.5–165.5°.

Anal. Calcd. for $C_{16}H_{13}O_3Cl$: C, 66.56; H, 4.54; Cl, 12.28. Found: C, 67.04; H, 4.38; Cl, 12.19.

3-(5-Bromo-2-ethoxyphenyl)phthalide. The reaction mixture consisted of 1.5 g. (0.01 mole) of phthalaldehydic acid dissolved in 25 ml. of 4:1 concd. sulfuric acid–water, with 2.0 g. (0.01 mole) of added *p*-bromophenetole. Following essentially the same procedure as outlined above for the chloro analog, there was obtained 3.1 g. (93%) of crude phthalide, yellow in color. Crystallization from glacial

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(7) A. Bistrzycki and Yessel de Schepper, *Ber.*, **31**, 2790 (1898).

(8) The majority of the elementary analyses reported here were performed by the Tiedcke Laboratory of Microchemistry.

(9) F. Thorpe, *Ber.*, **26**, 1261, 1795 (1893).

acetic acid gave 2.35 g. (71%) of fine white crystals, m.p. 175–176°.

Anal. Calcd. for $C_{16}H_{13}O_3Br$: C, 57.67; H, 3.94; Br, 23.98. Found: C, 57.91; H, 3.83; Br, 23.82.

3-(5-Chloro-2-hydroxyphenyl)phthalide. One and one-half grams (0.01 mole) of phthalaldehydic acid was dissolved in 18 ml. of 3:1 concd. sulfuric acid–water. This solution was cooled in an ice-water bath, and 1.28 g. (0.01 mole) of *p*-chlorophenol was added. After mechanically stirring the mixture for 2 hr. the cooling bath was removed and stirring was continued for an additional 2 hr. At this point the thick, milky emulsion was brought into a large volume of cold water, with vigorous stirring. A voluminous white solid separated and gradually settled out. The crude product was removed, washed thoroughly with cold water, and permitted to dry overnight. This gave a white powdery solid weighing 2.3 g. (88%). Recrystallization from ethanol yielded 1.83 g. (70%) of soft, glistening needles. An analytical sample melted at 163.5–164°.

Anal. Calcd. for $C_{14}H_9O_3Cl$; C, 64.51; H, 3.48; Cl, 13.60. Found: C, 64.64; H, 3.29; Cl, 13.73.

3-(5-Methyl-2-methoxyphenyl)phthalide. A solution of 1.5 g. (0.01 mole) of phthalaldehydic acid in 24 ml. of 3:1 concd. sulfuric acid–water was prepared. This was cooled by immersion in an ice-water bath, and 1.22 g. (0.01 mole) of *p*-methylanisole was then added. The mixture was mechanically stirred; after 3 hr. testing showed that the brown oil which had separated as a top layer would solidify in water. The entire reaction mixture was poured with stirring into a large volume of cold water. The gum which separated soon hardened to a yellow solid; when firm it was removed and thoroughly washed with cold water. Drying gave as crude product 2.55 g. (100%) of light yellow solid. Recrystallization from ethanol yielded 2.03 g. (80%) of white crystals, m.p. 120.5–121.5°.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.34; H, 5.71.

3-(5-Methyl-2-ethoxyphenyl)phthalide. This phthalide was synthesized by using 1.5 g. (0.01 mole) of phthalaldehydic acid and 1.34 g. (0.01 mole) of *p*-methylphenetole with 24 ml. of 3:1 concd. sulfuric acid–water as the condensing agent. The procedure followed was essentially the same as outlined for 3-(5-methyl-2-methoxyphenyl)phthalide. The crude reaction product weighed 2.42 g. (91%). Recrystallization from ethanol gave 1.98 g. (74%) of white needles. An analytical sample melted at 151–151.5°.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.09; H, 6.01. Found: C, 76.21; H, 5.92.

3-(2,4,6-Trichloro-3-hydroxyphenyl)phthalide. One and one-half grams (0.01 mole) of phthalaldehydic acid was dissolved in 20 ml. of 1:1 concd. sulfuric acid–20% fuming sulfuric acid. To this solution at room temperature was added 1.98 g. (0.01 mole) of 2,4,6-trichlorophenol, and the mixture mechanically stirred. The dispersed phenol reacted over a period of 3 hr. to give a yellow solution. The reaction vessel was then immersed in a water bath maintained at 60–70°, and stirring was continued for an additional 2 hr. The reaction mixture was poured into a large volume of cold water. The gum which separated hardened very slowly, but became brittle after standing overnight. The crude product, nearly white in color, weighed 3.0 g. (90%). Recrystallization from glacial acetic acid gave 2.6 g. (80%) of nearly white cubic crystals, m.p. 164.5–165°.

Anal. Calcd. for $C_{14}H_7O_3Cl_3$: C, 51.02; H, 2.14; Cl, 32.27. Found: C, 51.10; H, 1.98; Cl, 32.41.

Acknowledgment. Appreciation is expressed to William V. Floutz, Wyandotte Chemicals Corp., for the infrared data, and its interpretation.

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Unsaturated Lactams. II.[1] The Catalytic Dehydrogenation of α,β-Unsaturated Valerolactams to Pyridones[2]

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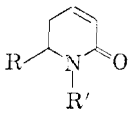
The fact that α,β-unsaturated lactams of type (I) are now readily available[1] induced us to extend the method used by Spath and Galinovsky for the synthesis of pyridones. These two workers found that six-membered saturated lactams could be smoothly dehydrogenated to the corresponding pyridones by treatment with palladium. In the present work, the unsaturated lactams (II) and (III) were dehydrogenated to the pyridones (IV) and (V), respectively.



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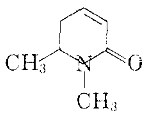

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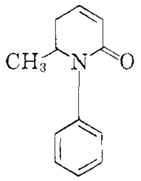

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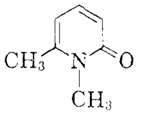
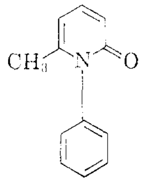


IV



V

As indicated in Table I, the dehydrogenation reactions were found to be temperature dependent.

TABLE I

Dehydrogenation of α,β-Unsaturated Valerolactams to Pyridones with 5% Palladium on Carbon

Solvent	B.P.	% Yield of IV	% Yield of V
Benzene	80°	30	—
Xylene	140°	40	28
p-(*n*-Propyl)anisole	247°	—	49

Catalytic dehydrogenation of α,β-unsaturated lactams can provide a route, therefore, to a variety of substituted pyridones which would be difficult to prepare by other routes.

EXPERIMENTAL[3]

1,6-Dimethyl-2-pyridone (IV). *Method A.* A well stirred suspension of 2 g. of 5% palladium on carbon, 50 ml. of xylene, and 10 g. (0.08 mole) of 1,6-dimethyl-5,6-dihydro-2-

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[1] For paper I see Maurice Shamma and Paul D. Rosenstock, *J. Org. Chem.*, **26**, 718 (1961).

[2] This research was supported in part by grant NSF-G10032 from the National Science Foundation.

[3] Elemental analyses were carried out by A. Bernhardt, Mulheim, Germany.