and 2.4 g. (0.04 mole) of urea was heated at 150° for 12 min. to yield a glass which was boiled with 50 ml. of water. Cooling gave a gelatinous material which was discarded. The liquor, *p*H 4, was acidified to *p*H 1 with hydrochloric acid to precipitate a heavy solid which was collected and then stirred with 150 ml. of methanol for 1.5 hr. After separation of a small amount of insoluble material, the methanol solution was concentrated to dryness and the residue suspended in butanone. A little insoluble material was removed and the liquor diluted with heptane to furnish a solid which was collected, dried and recrystallized from water and from butanone to furnish 1 g. (23%), m.p. 186–191°. The melting point varied with the rate of heat; however, the product showed good depression with 1-phenyl-3,5-pyrazolidinedione; in 0.1*N* sodium hydroxide, λ_{max} 290 (shoulder) and 256 mμ (ϵ = 4710 and 12,600).

Anal. Calcd. for $C_{10}H_9N_3O_3$: C, 54.79; H, 4.14; N, 19.17. Found: C, 54.46; H, 4.16; N, 19.20.

Acknowledgment. The author is indebted to Dr. Coy W. Waller for his assistance in the initiation of this work and to Dr. Richard T. Arnold for his suggestions regarding to mechanism proposed.

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Adducts of Halogenated Cyclopentadienes with Halogenated Quinones[1,2]

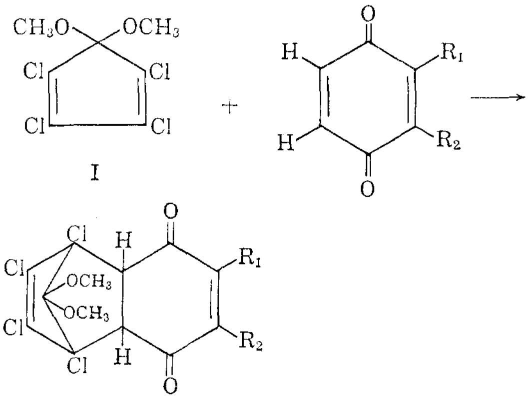
HENRY RAKOFF AND BRAD H. MILES[3]

Received October 26, 1960

The use of tetrachloro-substituted, conjugated, alicyclic dienes as reactants in the Diels-Alder Reaction has been known for some time. 1,2,3,4-Tetrachloro-1,3-cyclopentadiene,[4] tetrachlorocyclopentadienone,[5] and 5,5-dimethoxy-1,2,3,4-tetrachloro-1,3-cyclopentadiene (I)[6] are all known to undergo this reaction.

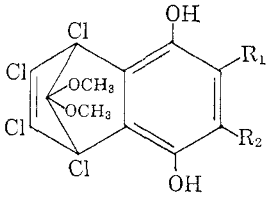
McBee, Diveley, and Burch[6] describe a method for preparing aromatic compounds by a sequence of reactions involving hydrolysis of the ketal and removal of the carbonyl bridge from adducts between I and various dienophiles. It was hoped that this sequence could be applied to the synthesis of chlorinated naphthoquinones. While this desire was not realized, some novel information on the chemical behavior of the adducts between I and chlorinated quinones was obtained.

The diene (I) was treated with *p*-benzoquinone, monochloroquinone, and 2,3-dichloroquinone to yield the expected adducts (II–IV). Attempts to react I with 2,5-dichloroquinone or with chloranil were unsuccessful.



II. $R_1 = R_2 = H$
III. $R_1 = H; R_2 = Cl$
IV. $R_1 = R_2 = Cl$

Attempts to hydrolyze the adducts to the carbonyl bridge compounds with sulfuric acid gave either no reaction or highly colored, pasty materials depending upon the concentration of the acid employed. Attempted hydrolysis of II with an acetic acid-hydrochloric acid mixture converted it to its enol isomer (V). Adducts III and IV were isomerized to their enol isomers, VI and VII, by refluxing the respective adducts in methyl alcohol containing pyridine.[7]



V. $R_1 = R_2 = H$
VI. $R_1 = H; R_2 = Cl$
VII. $R_1 = R_2 = Cl$

The diacetates and dibenzoates of enol isomers V, VI, and VII and the diethyl ethers of V and VI were prepared according to standard procedures.

The reaction of II with stannous chloride and hydrochloric acid resulted in reduction of the double bond in the quinone portion of the molecule. The carbonyl groups were not reduced, but the yellow color of the quinone was lost leaving the white compound VIII. The infrared spectrum of this compound is consistent with the presence of carbonyl groups and the absence of hydroxy groups. In addition, VIII reacted with 2,4-dinitrophenylhydrazine to form a bright yellow, bis-2,4-dinitrophenylhydrazone. The reduction of III or IV with

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(1) A portion of this work is taken from the M.S. thesis of Brad H. Miles.

(2) A portion of this work was presented before the Southwest Regional Meeting of the American Chemical Society. San Antonio, Tex., Dec., 1958.

(3) Present address: Dow Chemical Company, Freeport, Tex.

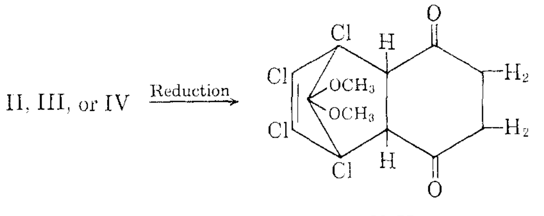
(4) E. T. McBee, R. K. Meyers, and C. F. Baranauckas, *J. Am. Chem. Soc.*, **77**, 86 (1955).

(5) J. S. Newcomer and E. T. McBee, *J. Am. Chem. Soc.*, **71**, 948 (1949).

(6) E. T. McBee, W. R. Diveley, and J. E. Burch, *J. Am. Chem. Soc.*, **77**, 385 (1955).

(7) E. Segel, R. E. Lidov, and J. Hyman, U. S. Pat. **2,584,140** (Feb. 5, 1952); *Chem. Abstr.*, **46**, 9591i (1952).

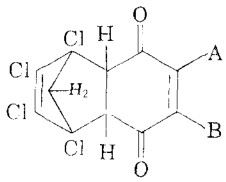
iron and acetic acid also yielded VIII. The method of mixed melting points, elemental analyses, formation of the same bis-2,4-dinitrophenylhydrazone, and comparison of infrared spectra all testify to the fact that the same compound VIII is produced by reduction of the three different adducts.



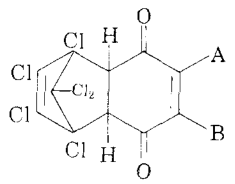
VIII

Reduction of II to the dione (VIII) is straight forward. Reduction of III or IV to VIII, however, requires replacement of chlorine by hydrogen. A similar type of replacement has been reported.[8] 3-Chloro-5-hydroxynaphthoquinone (3-chlorojuglone) is converted to 1,2,3,4-tetrahydro-5-hydroxy-1,4-naphthalenedione (β-hydrojuglone) by acidic stannous chloride.

The non-reactivity of diene I with 2,5-dichloroquinone and with chloranil led to a study of the reaction of hexachlorocyclopentadiene, 1,2,3,4-tetrachlorocyclopentadiene, and cyclopentadiene with these and the other chlorinated quinones employed. It was found that both hexachlorocyclopentadiene[9] and tetrachlorocyclopentadiene would form adducts with chloroquinone and with 2,3-dichloroquinone (IX-XII) but not with 2,5-dichloroquinone nor with chloranil. These observations are in accord with previous results[10] obtained when hexachlorocyclopentadiene was permitted to react with halogenated olefins. It was found then that hexachlorocyclopentadiene would not form an adduct with a halogenated olefin unless that olefin had at least one hydrogen on each of the doubly bonded carbon atoms. This observation lends support to the structures presented for the monochloro- and the 2,3-dichloroquinone adducts as against the alternative possibility in which the diene adds to the double bond holding the halogen.



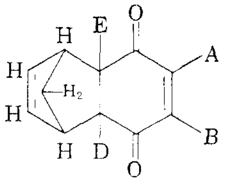
IX. A = Cl; B = H
X. A = B = Cl



XI. A = Cl; B = H
XII. A = B = Cl

It would appear at first though that the two allylic chlorines in hexachlorocyclopentadiene or the two allylic methoxy groups in dimethoxytetrachlorocyclopentadiene, which are not in the plane of the ring, would interact sterically with the chlorine on the double bonds of 2,5-dichloroquinone and chloranil. As tetrachlorocyclopentadiene also fails to react with these two quinones, however, it appears that the groups on the allylic position of the diene do not make possible nor inhibit this reaction.

The adducts of cyclopentadiene with quinone[11] and with chloranil,[11,12,13] are recorded in the literature while the adducts with chloroquinone (XIII) and with 2,3-dichloroquinone (XIV) have not been reported previously. An unsuccessful attempt to prepare the adducts between cyclopentadiene and 2,5-dichloroquinone (XV) or 2,6-dichloroquinone (XVI), has been reported by Gaertner.[13]



	A	B	D	E
XIII.	Cl	H	H	H
XIV.	Cl	Cl	H	H
XV.	Cl	H	Cl	H
XVI.	Cl	H	H	Cl

EXPERIMENTAL[14]

Hexachlorocyclopentadiene was donated by the Hooker Chemical Corporation while the Velsicol Chemical Corporation supplied the dicyclopentadiene. 2,5-Dichloroquinone and chloranil were purchased from Eastman Organic Chemicals. 1,2,3,4-Tetrachlorocyclopentadiene,[4] 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene,[5] 2-chloroquinone,[15] 2,3-dichloroquinone,[16] 2,6-dichloroquinone,[17] and adduct II[6] were prepared by published procedures.

III. Between 2,5-dichloroquinone and cyclopentadiene. Freshly cracked cyclopentadiene (1.8 g.; 0.026 mole) and 2,5-dichloroquinone (4 g.; 0.02 mole) were mixed in benzene solution (25 ml.) and heated at the reflux temperature for 2 hr. The cool solution was diluted with petroleum ether (b.p. 60–70°) (100 ml.) and a pale yellow solid (1.75 g., m.p. 113–114°) was obtained by filtration. A second crop (3.35 g., m.p. 113–114°) was obtained by evaporating the filtrate almost to

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[8] D. B. Bruce and R. H. Thomson, *J. Chem. Soc.*, 2759 (1952).

[9] R. E. Lidov, J. Hyman, and E. Segel, U. S. Pat. **2,584,139** (Feb. 5, 1952) claim the preparation of XI and XII but give no physical constants nor elemental analyses.

[10] E. T. McBee, H. Rakoff, and R. K. Meyers, *J. Am. Chem. Soc.*, **77**, 4427 (1955).

[11] E. C. Ladd, Canadian Pat. **501,628** (Apr. 20, 1954); *Chem. Abstr.*, **50**, 8126e (1956).

[12] J. Hyman, U. S. Pat. **2,507,207** (May 9, 1950); *Chem. Abstr.*, **44**, 9617f (1950).

[13] R. Gaertner, *J. Am. Chem. Soc.*, **76**, 6150 (1954).

[14] All melting points are uncorrected. Carbon and hydrogen determinations were run by Weiler and Strauss Microanalytical Laboratory, Oxford, England, and by the Galbraith Microanalytical Laboratory, Knoxville, Tenn. Chlorine determinations were run by the authors and by the State Chemist's Laboratory.

(15 L. F. Fieser, *Experiments in Organic Chemistry*, 2nd Ed., D. C. Heath and Co., New York, 1941, p. 228.

[16] J. B. Conant and L. F. Fieser, *J. Am. Chem. Soc.*, **45**, 2204 (1923).

[17] F. Kehrmann and W. Tiesler, *J. prakt. chem.* [2], **40**, 481 (1889).

TABLE I

PREPARATION OF ADDUCTS

Diene	Adduct	Reaction			Rextn.	M.P.	Conv.	% Cl	
		Solvent	Temp.	Time	Solvent			Calcd.	Found
			I. Between Chloroquinone and						
Cyclopentadiene	XIII	Skelly B[a]	R.T.	3 min.	Skelly B	63–64°	77%	16.99	16.96; 16.85
Tetrachlorocyclopentadiene	IX	Benzene	Reflux	8 hr.	Ethanol	148.5–149°	99%	51.18	50.87; 51.00
Hexachlorocyclopentadiene	XI	None	Heated to 160°		Skelly B	177–178°	69%	59.76	59.64; 59.65
Dimethoxytetrachlorocyclopentadiene	III	Toluene	Reflux	16 hr.	Ethanol	155.5–157°	81%	43.62	43.89[b]
			II. Between 2,3-Dichloroquinone and						
Cyclopentadiene	XIV	Benzene	R.T.	16 hr.	Skelly B	109–110°	74%	29.17	28.90; 28.98
Tetrachlorocyclopentadiene	X	Benzene	R.T.	16 hr.	Skelly B	168–169°	69%	55.86	55.44; 55.52
Hexachlorocyclopentadiene	XII	None	Heated to 138°		Skelly B	177–179°	88%	63.07	62.46; 62.50
Dimethoxytetrachlorocyclopentadiene	IV	Toluene	Reflux	42 hr.	Ethanol	204–205.5°	54%	48.25	47.83[c]

[a] Petroleum ether (b.p. 60–70°). [b] C and H analysis; Calcd.: C, 38.41; H, 2.23. Found: C, 38.92, 38.94; H, 2.50, 2.52. [c] C and H analysis: Calcd.: C, 35.41; H, 1.83. Found: C, 35.58, 35.60; H, 2.29, 2.04.

dryness and diluting with petroleum ether (50 ml.). The analytical sample, XV, m.p. 113–114°, was prepared by recrystallizing the crude material twice from petroleum ether (once with Darco); yield (crude), 93%.

Anal. Calcd. for $C_{11}H_8Cl_2O_2$: C, 54.35; H, 3.32; Cl, 29.17. Found: C, 54.55, 54.60; H, 3.11, 3.09; Cl, 29.39, 29.05.

With these same two reagents Gaertner[13] reported the preparation of a compound, m.p. 113.5–115.5° for which good analytical data could not be obtained.

IV. *Between 2,6-dichloroquinone and cyclopentadiene.* Freshly cracked cyclopentadiene (0.85 g. 0.012 mole) and 2,6-dichloroquinone (2.2 g.; 0.012 mole) were mixed in benzene (5 ml.) and an exothermic reaction ensued. About an hour later the solution was diluted with petroleum ether (20 ml.) and cooled in a Dry Ice–acetone bath. A pale yellow solid (2.7 g.) was filtered, m.p. 70.5–72°. The analytical sample, XVI, m.p. 72.5–73.5°, was prepared by recrystallizing this material twice from petroleum ether (once with Darco); yield (crude), 93%.

Anal. Calcd. for $C_{11}H_8Cl_2O_2$: C, 54.35; H, 3.32; Cl, 29.17. Found: C, 54.35, 54.48; H, 3.14, 3.37; Cl, 29.28, 29.08.

With these same two reagents, Gaertner[13] obtained a compound, m.p. 138–140°, which decomposed rapidly on standing and for which good analytical data could not be obtained. Our product, m.p. 72.5–73.5°, whose analysis checked well with the calculated values, decomposed slowly; after two weeks the melting point had dropped to 64–65°. The difference in the products obtained may be due to the difference in reaction time employed and to the fact that Gaertner took cyclopentadiene and 2,6-dichloroquinone in a 1.5:1 ratio while we took them in a 1:1 ratio.

Preparation of enol isomers. A. *Of Adduct* III. *Preparation of compound* VI. *Typical Preparation.* A mixture of adduct III (5 g.; 0.012 mole), methanol (50 ml.), and pyridine (15 drops) was heated under reflux for 12 hr. The solution was neutralized with sulfuric acid and reduced to about one-fourth the original volume by boiling at atmospheric pressure. Water was added to precipitate the product which was extracted into boiling petroleum ether. This extract was filtered, reduced in volume by boiling, and cooled in an ice bath. The reddish-white precipitate which formed was recrystallized from petroleum ether (Darco added) and yielded the enol isomer, VI, m.p. 132–134°; conversion was 48%.

Anal. Calcd. for $C_{13}H_9Cl_5O_4$: C, 38.41; H, 2.23; Cl, 43.62. Found: C, 38.50, 38.71; H, 2.65, 2.56; Cl, 43.13.

B. *Of adduct IV. Preparation of compound* VII. M.p. 154.5–156°; conversion; 70%.

Anal. Calcd. for $C_{13}H_8Cl_6O_4$: C, 35.41; H, 1.83; Cl, 48.25. Found: C, 35.86, 36.09; H, 1.79, 1.54; Cl, 47.95.

C. *Of adduct* II. *Preparation of compound* V. M.P. 203–204°; conversion, 90%.

Anal. Calcd. for $C_{13}H_{10}Cl_4O_4$: C 41.97; H, 2.71; Cl, 38.12. Found: C, 41.78, 41.93; H, 3.03, 3.15; Cl, 38.19, 38.38.

Preparation of derivatives of the enol isomers. A. *Benzoates.* The dibenzoates were prepared by treating 0.5-g. quantities of the enol isomers with dry pyridine (3 ml.) and benzoyl chloride (2 ml.). After the exothermic reaction had subsided, concentrated hydrochloric acid was added. An oil separated from the solution but it solidified on stirring with a glass rod. The crystals were filtered, washed with 5% sodium carbonate solution, and recrystallized from methanol. Conversions of 90% were realized.

Dibenzoate of enol isomer V. M.p. 228–230°.

Anal. Calcd. for $C_{27}H_{18}Cl_4O_6$: C, 55.88; H, 3.13; Cl, 24.44. Found: C, 55.83, 55.61; H, 3.23, 3.34; Cl, 24.44, 24.17.

Dibenzoate of enol isomer VI. M.p. 204.5–206°.

Anal. Calcd. for $C_{27}H_{17}Cl_5O_6$: C, 52.75; H, 2.79; Cl, 28.84. Found: C, 52.93, 53.12; H, 2.72, 2.80; Cl, 28.96.

Dibenzoate of enol isomer VII. M.p. 230°.

Anal. Calcd for $C_{27}H_{16}Cl_6O_6$: C, 49.96; H, 2.48; Cl, 32.44. Found: C, 50.58, 50.03; H, 2.61, 2.60; Cl, 32.77.

B. *Acetates.* The diacetates were prepared by treating 2-g. quantities of the enol isomers with 2 ml. of acetic anhydride and 1 drop of concentrated sulfuric acid. After the exothermic reaction had subsided, water was added to precipitate the product and to hydrolyze excess acetic anhydride. The product was filtered, washed with water, and recrystallized from petroleum ether. Conversions ranged from 83 to 98%.

Diacetate of enol isomer V. M.p. 161–163°.

Anal. Calcd. for $C_{17}H_{14}Cl_4O_6$: C, 44.76; H, 3.09; Cl, 31.09. Found: C, 44.85, 45.08; H, 3.37, 3.12; Cl, 31.01, 31.30.

Diacetate of enol isomer VI. M.p. 165–166°.

Anal. Calcd. for $C_{17}H_{13}Cl_5O_6$: C, 41.62; H, 2.67; Cl, 36.13. Found: C, 40.62, 40.74; ,H 3.06, 3.06; Cl, 35.68.

Diacetate of enol isomer VII. M.p. 160–161°.

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

VAUGHN W. FLOUTZ

Received November 1, 1960

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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(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.

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