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Charge-transfer Interaction and Chemical Reaction. V. Reaction of *o*-Phenylenediamine with Chloranil

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The reaction of *o*-phenylenediamine with chloranil in ether was studied by measuring visible and ultraviolet absorption spectra at various temperatures between −78 °C and room temperature. Dehydrogenation of *o*-phenylenediamine by chloranil occurred, *o,o'*-diaminoazobenzene, 2,3-diaminophenazine and tetrachlorohydroquinone being produced as main reaction products. It was suggested that the reaction involves *o*-benzoquinone di-imine as an intermediate. For the sake of confirmation, *o*-benzoquinone di-imine was prepared by an independent method, and its reaction with *o*-phenylenediamine was examined. The difference in reactivity of isomeric phenylenediamines toward chloranil is discussed.

The reactions of chloranil (CA) with such aromatic amines as aniline, *s*-triaminobenzene, *m*-phenylenediamine, *p*-phenylenediamine, and *N,N*-dimethyl-*p*-phenylenediamine have been studied, special attention being paid to charge-transfer interaction.[1a–d] Spectrophotometric studies show that substitution reaction occurs for the *meta*-substituted derivatives of aniline in ether or acetone *via* inner complex (σ-complex) formed through outer complexes, while the reaction proceeds for the *para*-substituted derivatives in the mixed solvent, ether–isopropyl alcohol (3: 1), through ionic species produced from the outer complex. The difference in the reaction mechanism between the *m*- and *p*-substituted derivatives of aniline was explained in terms of the nonbonding electron density on the amino group.

The reaction of *ortho*-substituted derivatives of aniline with CA remains to be solved. We have studied spectrophotometrically the reaction between *o*-phenylenediamine (*o*-PD) and CA in ethyl ether. The results are given in this paper.

Experimental

Materials. Chloranil was purified by column chromatography (benzene–calcium carbonate) in order to eliminate acidic impurities,[2] and then recrystallized twice from acetone. *o*-Phenylenediamine was purified by repeated sublimation *in vacuo*.

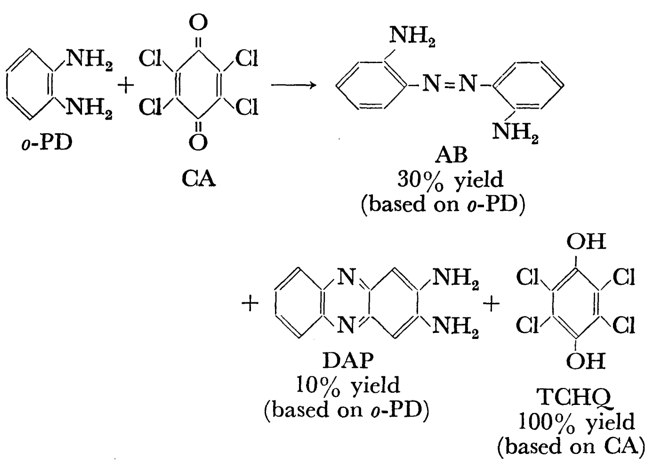
Measurements. The ultraviolet and visible absorption spectra were measured with a Hitachi two-wavelength double beam spectrophotometer model 356 and also with a Hitachi 124 spectrophotometer. Donor and acceptor solutions were prepared separately and mixed together just before each measurement. For measurements at low temperatures, the sample was cooled with a dry-ice methanol mixture in a quartz Dewar vessel designed for spectroscopic measurements. The temperature was measured by a copper-Constantan thermocouple.

Isolation and Identification of the Reaction Products. *o*-Phenylenediamine (0.616 g) in 60 ml ether and chloranil (0.702 g) in 500 ml ether (the mole ratio, [*o*-PD]: [CA]= 2: 1) were mixed together at room temperature and kept for five days.[3] Precipitate (I) produced was collected by filtration, yield 0.175 g. The filtrate was evaporated to dryness under reduced pressure, 0.892 g of powder (II) being obtained. No component molecules were detected in I and II judging from their thin layer chromatograms. I and II were independently chromatographed on alumina (benzene–acetone mixed solvent as an elute). Three main fractions were collected, *i.e.*, a yellow eluent in I, a red one in II, and a colorless one in II. They were further purified by thin layer chromatography and identified as 2,3-diaminophenazine (DAP) (yellow eluent in I), *o,o'*-diaminoazobenzene (AB) (red eluent in II), and tetrachlorohydroquinone (TCHQ) (colorless eluent in II). The yields of DAP, AB, and TCHQ were respectively 10, 30, and 100% of theoretical values. In addition to the three main products, seven or more other minor products were formed. However, they were not identified because of small quantities and difficulty in purification. Identification of DAP and TCHQ was made by comparing their mass, IR and electronic absorption spectra with those of authentic samples. Electronic absorption spectra (in ethyl ether); DAP: λ_{max} 450 nm (ε=17000), 425 nm (ε=21000). TCHQ: λ_{max} 310 nm (ε=6600). Identification of AB was made by mass, IR and electronic absorption spectra and elemental analysis. Mass spectra; *m/e* 212 (M^+), 92 ($M^+-C_6H_4(NH_2)N_2$). IR spectra; 3430, 3350 cm^{-1} (NH stretching), 1560 cm^{-1} (N=N stretching). Electronic absorption spectra; λ_{max} 470 nm (ε=1580), 312 nm (ε=1580), 265 nm (ε=2170). Found: C, 67.39; H, 6.24; N, 26.37%. Calcd for $C_{12}H_{12}N_4$: C, 67.92; H, 5.66; N, 26.42%.

Synthesis of o-*Benzoquinone Di-imine.*[4] Freshly prepared lead dioxide[5] (350 mg) and anhydrous sodium sulfate (100 mg) baked beforehand for 30 min were added to an ether solution (30 ml) of *o*-PD (1.7 mg) under cooling with ice-salt and then vigorously stirred for five min. The solution was filtered, and the yellow filtrate was used directly. All the procedures were performed under anhydrous conditions. The yellow compound in the solution thus obtained seems to be spectroscopically of high purity, and is assigned to *o*-benzoquinone di-imine (*o*-BQDI), since the absorption spectrum of the yellow solution (λ_{max} 352 nm, ε=1300[6]) is similar to that of the corresponding isoelectronic *o*-benzoquinone.[7] *o*-BQDI obtained in ether solution was fairly stable only when kept below 0 °C in a dilute solution, but it was unstable in a concentrated solution because of its gradual conversion into AB. This prevented us from carrying out its isolation.

Results and Discussion

The reaction of *o*-PD with CA in ether at room temperature yielded AB, DAP, and TCHQ as main products.



CA was quantitatively converted into TCHQ. This indicates that the dehydrogenation reaction of *o*-PD by CA occurs at first and the oxidized *o*-PD undergoes further reactions to yield AB and DAP.[8] The reaction course was followed by electronic absorption measurements under controlled temperature.

Spectroscopic Course of the Reaction in o-*PD–CA System.* After mixing an ether solution of *o*-PD (3.0×10^{-3} M) with one of CA (1.5×10^{-3} M) at −78 °C, the change of absorption spectra was measured at various temperatures. Figure 1 shows the spectral change measured below −50 °C. The 708 and 460 nm bands which appear immediately after mixing were assigned to the outer complex for the following reasons. (a) The 708 nm band is interpretated to be a charge-transfer (CT) band of the *o*-PD–CA complex from a comparison of its position with the CT band positions observed for the CA and trinitrobenzene complexes with several aromatic amines. (b) The intensities of both bands change parallel with temperature. Their intensities decrease monotonically with increasing temperature between −78 and −50 °C because of the decrease in the equilibrium constant of the outer complex.

Figure 2 shows the spectral change of the reaction system measured above −50 °C. The spectra measured at higher temperatures have new bands at 470 nm and around 360 nm[9] and show an isosbestic point at 590 nm. The bands are assigned to AB and *o*-BQDI, respectively. Figure 3 shows the time dependence of the absorption spectrum measured at room temperature ([*o*-PD]$=2.0 \times 10^{-3}$ M, [CA]$=1.0 \times 10^{-3}$ M). The intensity of the AB band at 470 nm increases slowly with time. The 430 nm band due to DAP appears about 13 hr after mixing. The 360 nm band was observed clearly only 6 hr after mixing. The increase of TCHQ band peaking at 310 nm could not be followed because of an overlap with the absorption of component molecules and reaction products.

Role of Outer Complex in the Reaction. It is of interest to see whether the outer complex takes part in the main reaction as a reaction intermediate or exists only in a side reaction. In this connection, Garbutt and Gerrard and Farrell and Ngo demonstrated by kinetic study that the outer complex directly takes part in the main reaction in the tricyanovinylation reaction of aniline and *N*,*N*-dimethylaniline with tetracyanoethylene.[10] We could not clarify the role of the outer complex in the present system, but it is probable that the reaction proceeds through the outer complex in view of the correspondence of the decrease of the outer complex band and the increase of AB band (Fig. 2).

o-*Benzoquinone Di-imine as a Reaction Intermediate.* The present result indicates that *o*-benzoquinone diimine (*o*-BQDI) can take part in the formations of AB and DAP as a reaction intermediate. For the sake of clarification, we attempted to prepare *o*-BQDI by another route and succeeded in obtaining *o*-BQDI fairly stably in an ether solution.[11] The absorption maximum of *o*-BQDI at 352 nm was found to be in good agreement with the shoulder around 360 nm appearing in the reaction of *o*-PD with CA.

o-BQDI alone produced AB, though very slowly. It was found that the addition of *o*-PD greatly accelerated the AB formation reaction. This indicates that AB is produced by the interaction between the

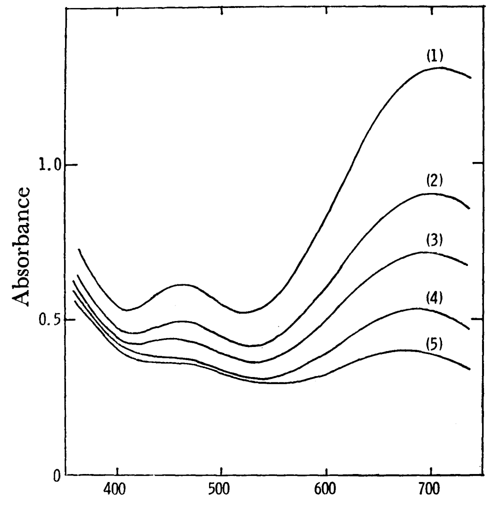


Fig. 1. The change of the outer complex bands with temperature in *o*-PD–CA system in ethyl ether. [*o*-PD]$=3.0 \times 10^{-3}$ M, [CA]$=1.5 \times 10^{-3}$ M.
(1) −78 °C, (2) −72 °C, (3) −65 °C, (4) −55 °C, (5) −50 °C.

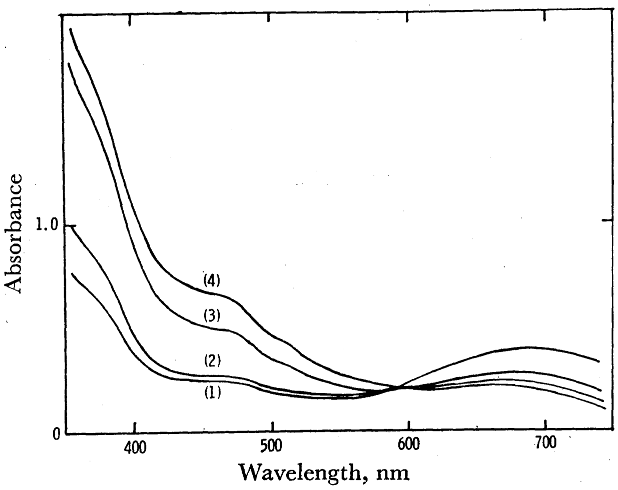


Fig. 2. Spectroscopic course of the reaction in *o*-PD–CA system in ethyl ether measured at several temperatures. [*o*-PD]$=3.0 \times 10^{-3}$ M, [CA]$=1.5 \times 10^{-3}$ M.
(1) −44 °C, (2) −31 °C, (3) −20 °C, (4) −7 °C.

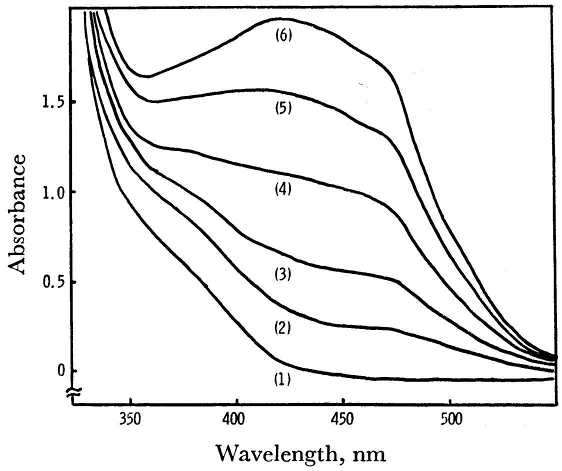


Fig. 3. Spectroscopic course of the reaction in *o*-PD–CA system in ethyl ether measured at room temperature. [*o*-PD]$=2.0\times10^{-3}$ M, [CA]$=1.0\times10^{-3}$ M.
(1) 5 min, (2) 1 hr, (3) 2 hr 26 min, (4) 6 hr 13 min, (5) 13 hr 15 min, (6) 21 hr after mixing.

intermediate *o*-BQDI and *o*-PD in the reaction of *o*-PD with CA. The time dependence of the absorption spectrum in *o*-BQDI–*o*-PD system in ethyl ether measured at room temperature is shown in Fig. 4. This figure shows that with the decreasing intensity of the *o*-BQDI band at 352 nm, the intensity of AB band at 470 nm increases with the isosbestic point at 380 nm. It was found that DAP was produced when the solution of *o*-BQDI–*o*-PD system was left to stand for 24 hr. Thus, we can conclude that *o*-BQDI takes part in the reaction of *o*-PD with CA as an intermediate.

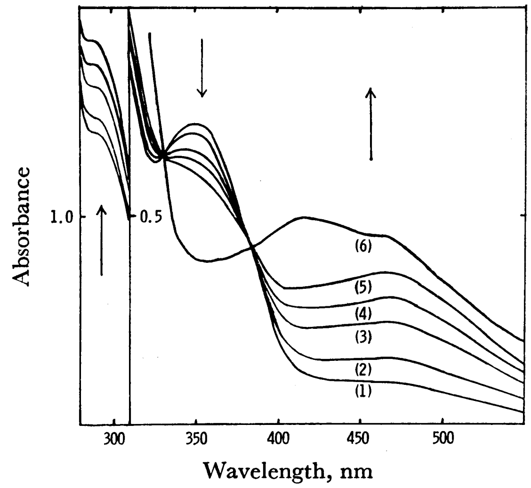
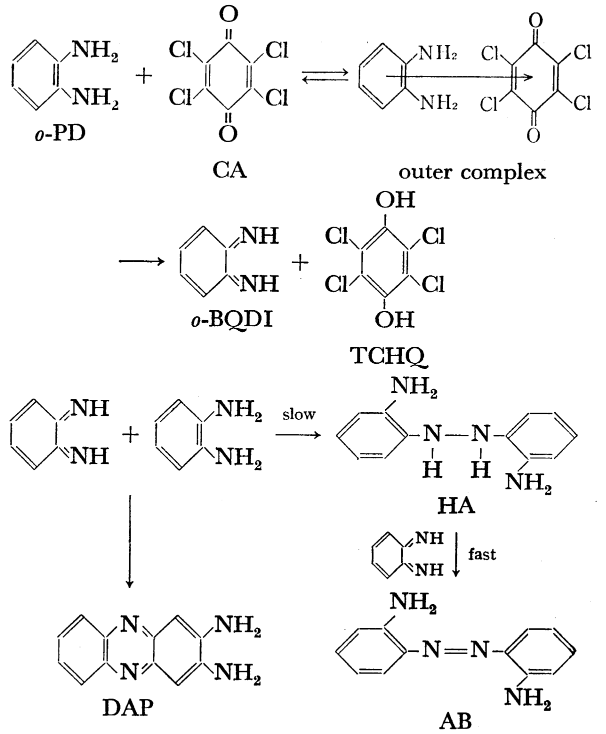
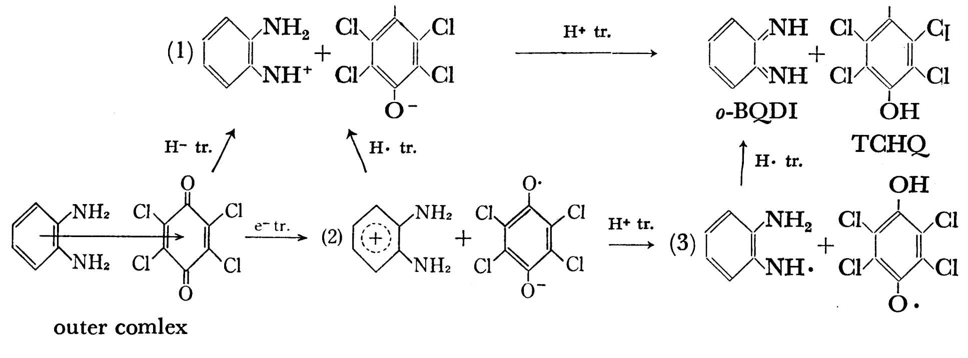


Fig. 4. Spectroscopic course of the reaction in *o*-BQDI–*o*-PD system in ethyl ether measured at room temperature. [*o*-BQDI]$=3.8\times10^{-3}$ M, estimated from the initial concentration of *o*-PD in the synthesis of *o*-BQDI, [*o*-PD]$=9.5\times10^{-4}$ M.
(1) 1 min, (2) 8 min, (3) 41 min, (4) 85 min, (5) 164 min, (6) 24 hr after mixing.

Reaction Scheme. The reaction scheme for the formation of AB, DAP, and TCHQ in the reaction of *o*-PD with CA might be shown as follows. The formation of AB through *o*,*o*'-diaminohydrazobenzene (HA) was suggested from its similarity with the reactions of *p*-benzoquinone di-imine with several aromatic amines.[12]



Details of the dehydrogenation process of *o*-PD by CA have not been clarified in the present study. The following two mechanisms have currently been accepted for the dehydrogenation mechanism by benzoquinone and its derivatives.[13] (1) Initial hydride ion abstraction from the donor compound D by CA to produce intermediate D(–H)$^+$ and CA semiquinone anion. (2) Initial electron transfer from D to CA to produce D cation radical and CA anion radical. In addition to these mechanisms, we considered a third one which involves semiquinone radical.[14] The possible reaction mechanisms can be described as follows:



Spectrophotometrically, we could detect no transient species in the above scheme[15] probably due to the following reasons. (1) The reaction consists of the initial rate-determining formation of these intermediate species, followed by the rapid formations of *o*-BQDI and TCHQ. (2) The absorption bands of these intermediate species are covered with those of the reaction products and component molecules. (3) These species are too unstable in the presence of air to be detected by electronic absorption spectra.

Differences of Reactivity of Isomeric Phenylenediamines toward Chloranil. A series of studies on the reactions of CA with *o*-, *m*-, and *p*-phenylenediamines in ethyl ether[1a–d] lead to the conclusion that their reaction mechanisms differ from one another, although in all cases the outer complexes are involved as intermediates. Dehydrogenation reaction occurs for the *o*-PD–CA system, substitution reaction through inner complex for the *m*-PD–CA system, and formation of stable ion-pair salts $p\text{-PD}^{+}\text{CA}^{-}$ and $(p\text{-PD})_2{}^{+}\text{CA}^{-}$ for the *p*-PD–CA system. The differences in the reactions can be explained by considering the following three competitive factors, (1) the electron-donating ability of the nonbonding electron on the amino group, (2) the facility of dehydrogenation of amino hydrogen, (3) the stability of the ion-pair salts. The nonbonding electron density on the amino nitrogen is larger in *m*-PD than in *o*-PD and *p*-PD.[1c] Thus, *m*-PD forms the inner complex with CA much easier, leading to the subsequent substitution reaction. In addition to the higher electron density on the amino nitrogen of *m*-PD, its dehydrogenation is less probable since the *m*-isomeric benzoquinone di-imine structure is impossible. The dehydrogenation reaction by CA is conceivable both in *o*-PD–CA and *p*-PD–CA systems. However, because of the stability of the ion-pair salts formed between *p*-PD and CA, salts formation reactions occur preferentially in the *p*-PD–CA system. We could not obtain the ion-pair salts in *o*-PD–CA and *m*-PD–CA systems using several solvents, showing the instability of the salts. Thus, the ion-pair salt is unstable and dehydrogenation occurs relatively easily for the *o*-PD–CA systems.[13] Reactivity factors are summarized in the Table 1. It should be noted that these discussions hold when one uses ethyl ether as a solvent.

Table 1. Factors regulating the reactivities of *o*-, *m*- and *p*-phenylenediamines in ethyl ether

	Nonbonding electron density on amino nitrogen	Facility of dehydrogenation	Stability of ion-pair salt
o-PD	relatively small	large[a]	unstable
m-PD	relatively large[b]	small	unstable
p-PD	relatively small	large	stable[c]

a) This leads to the dehydrogenation reaction in the *o*-PD –CA system. b) This leads to the substitution reaction in the *m*-PD –CA system. c) This leads to the ion-pair salts formation in the *p*-PD –CA system.

References and Notes

1) a) Part I: T. Nogami, K. Yoshihara, H. Hosoya, and S. Nagakura, *J. Phys. Chem.*, **73**, 2670 (1969); b) Part II: T. Yamaoka and S. Nagakura, This Bulletin, **43**, 355 (1970); c) Part III: T. Nogami, T. Yamaoka, K. Yoshihara, and S. Nagakura, *ibid.*, **44**, 380 (1971); d) Part IV: T. Nogami, K. Yoshihara, and S. Nagakura, *ibid.*, **45**, 122 (1972).

2) T. Natuume, Y. Shirota, H. Hirata, S. Kusabayashi, and H. Mikawa, *Chem. Commun.*, **1969**, 289.

3) The reaction seemed to be completed in five days.

4) T. Nogami, T. Hishida, Y. Shirota, and H. Mikawa, *Chem. Lett.*, **1973**, 1019.

5) L. C. Newell and R. W. Maxon, "Inorganic Syntheses," Vol. 1, p. 45 (1939).

6) Estimated from the initial concentration of *o*-PD in the synthesis of *o*-BQDI.

7) H. Mason, *J. Amer. Chem. Soc.*, **70**, 138 (1948).

8) The oxidation of *o*-PD with AgO, (B. Ortiz, P. Villanueva, and F. Walls, *J. Org. Chem.*, **37**, 2748 (1972)), FeCl_3, (F. Ullmann and F. Mauthner, *Ber.*, **35**, 4302 (1902). F. Ullmann and J. Gnaedinger, *ibid.*, **45**, 3437 (1912)), lead tetraacetate, (K. Nakagawa and H. Onoue, *Tetrahedron Lett.*, **1965**, 1433. K. Nakagawa and H. Onoue, *Chem. Commun.*, **1965**, 396), and PbO_2 (R. Willstätter and A. Pfannenstiel, *Ber.*, **38**, 2350 (1905)), has been studied by several authors, AB, DAP and 1,4-dicyanobutadiene being reported as the reaction products.

9) This band appears as a shoulder because of the existence of a strong band below 350 nm.

10) S. Garbutt and D. L. Gerrard, *J. Chem. Soc. Perkin II*, **1972**, 782. P. G. Farrell and P. Ngo, *ibid.*, **1973**, 974.

11) R. Willstätter *et al.* postulated that they obtained *o*-BQDI, but their assignment was uncertain, see Ref. 8.

12) J. F. Corbett, *J. Chem. Soc., B*, **1969**, 818. J. F. Corbett and E. P. Gamson, *J. Chem. Soc. Perkin II*, **1972**, 1531, and papers cited therein.

13) E. A. Braude, L. M. Jackman, and R. P. Linstead, *J. Chem. Soc.*, 3548 (1954). E. M. Kosower, "Progress in Physical Organic Chemistry," ed. by S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Interscience Publishers, N. Y. (1965), p. 81.

14) We considered this mechanism from our observation that the semiquinone radical is involved in the *p*-phenylenediamine–CA system in ether–isopropyl alcohol (3: 1) mixed solvent at low temperatures.

15) The absorption peak positions of semiquinone anion, CA anion radical and semiquinone radical are as follows: semiquinone anion: λ_{max} 330 nm; CA anion radical: λ_{max} 417, 455 nm; semiquinone radical: λ_{max} 395, 415, 435, 462 nm. Semiquinone anion was obtained by the reaction of equimolar ratios of TCHQ and KOH in ethanol. Dianion ($\text{O}^{-}\text{C}_6\text{Cl}_4\text{O}^{-}$) was obtained ($\lambda_{\text{max}}$ 350 nm) with the use of excess KOH.

16) It is well known that the *o*-, *m*-, and *p*-phenylenediamines show important differences in chemical properties, and that *o*-PD is distinguished by the facility with which it gives rise to condensation reactions to heterocyclic compounds. "Chemistry of Carbon Compounds," vol. III, ed. by E. H. Rodd, Elsevier Publishing Company, Amsterdam, Houston, London, New York (1954), p. 224.