[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE OXIDATION OF TRICHLOROPHENOL[1]

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In the preceding paper on the oxidation of halogenated pyrogallol derivatives[2] it has been shown that the hypothesis of the transitory existence of unsaturated radicals containing univalent oxygen, an hypothesis originally propounded as a mechanism for the decompositions of certain phenol salts, can also be used to explain the effect of oxidizing agents on the phenols used there.

It is the purpose of the present paper to set forth the result of similar work on *sym.*trichlorophenol. It is believed that an even stronger case can be made out here for the explanation already given, as there seems to be no other mechanism which can explain as easily the facts observed.

Before this work was started, the behavior of trichlorophenol toward oxidizing agents seemed to be well understood, as five papers[3] had been published, each of which gave 2,6-dichloroquinone as the only product isolated. Faust had used nitric acid, both Weselsky and Levy had used "nitrous acid gas," and Kehrmann and Tiesler, as well as Ling, had used chromium trioxide.

Kehrmann and Tiesler, using a 20% excess of chromium trioxide, reported an almost quantitative yield of dichloroquinone. Ling, however, had observed the formation of a by-product. His crude dichloroquinone, when reduced by sulfur dioxide, gave 2,6-dichlorohydroquinone and certain black nodules in small amount. These nodules, on treatment with alcohol, gave a yellow substance melting at 117–120° which, on recrystallization from ligroin, melted at 125°. 2,6-Dichloroquinone melts at 121°. Ling stated that this new substance was being investigated further, but no account of the work seems to have been published.

Accordingly, the experiments with oxides of nitrogen and with chromium trioxide were repeated. The first method proved to be very destructive unless carefully controlled so that it was abandoned.

The action of chromium trioxide was next investigated, using the technique of Ling and the 20% excess of Kehrmann and Tiesler, with the result that Ling's results were duplicated. The product of the action of chromium trioxide in glacial acetic acid under our conditions was an initial

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[1] The work described in this paper formed part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Minerva Morse in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1925.

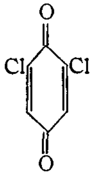
[2] Hunter and Levine, THIS JOURNAL, **48**, 1608 (1926).

[3] (a) Faust, *Ann.*, **149**, 153 (1869). (b) Weselsky, *Ber.*, **3**, 646 (1870). (c) Levy, *Ber.*, **16**, 1444 (1883). (d) Kehrmann and Tiesler, *J. prakt. Chem.*, [2] **40**, 481 (1889). (e) Ling, *J. Chem. Soc.*, **61**, 559 (1892).

yield of 27% of 2-6-dichloroquinone I (m. p., 121°) in a pure state, and 62% of a mixture of this substance with another quinone, the 2-(2′,4′,6′-trichlorophenoxy)-6-chloro-*p*-benzoquinone II, which melted at 134–135° when finally obtained pure.

The separation and distinguishing of these two substances from each other was a very perplexing task, since they resemble each other rather closely in appearance. Separation was finally accomplished by sublimation, the dichloroquinone subliming much more readily.

The use of lead dioxide in dry benzene produced another new oxidation product, the 2,6-di-(2′,4′,6′-trichlorophenoxy)-*p*-benzoquinone III. It is of considerable importance that all three products are formed by this last reagent, together with amorphous material resembling in many respects the polydichlorophenylene oxide obtained before from the salts of the phenol, but differing in its lower halogen content and considerable solubility in ether.[4] This is in striking contrast to the effect of lead dioxide in glacial acetic acid, which gives only the monophenoxyquinone II, in high yield.



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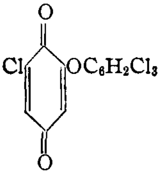

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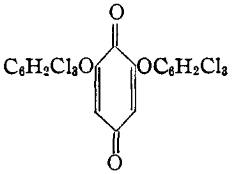

III

Constitution of the Oxidation Products

2,6-Dichloroquinone.—The identification of this well-known substance presented no difficulty after means were found to separate it from the monophenoxyquinone. For the sake of certainty, a sample was prepared from 2,6-dichloro-*p*-phenylenediamine, and the properties of the two were carefully compared.

2-(2′,4′,6′-Trichlorophenoxy)-6-chloro-*p*-benzoquinone II.—The composition and molecular weight of this substance showed that it contained four chlorine atoms for two benzene rings. It could not be mistaken for the tetrachlorodiphenoquinone of Magatti,[5] as this is a red crystalline substance which contains but two atoms of oxygen for two rings, instead of the three oxygens present in ours.

The presence of a quinoid structure in II was shown by analysis for quinonoid oxygen, and by reduction to a hydroquinone of like molecular weight which could be acetylated to a diacetyl derivative, or reoxidized in characteristic fashion to the original material. The content of quinonoid oxygen is 9.46%, as against 18.01 for dichloroquinone; hence, only one ring has the quinonoid structure.

[4] Compare Hunter and Seyfried, This Journal, **43**, 151 (1921).

[5] Magatti, *Ber.*, **13**, 225 (1880).

Its general resemblance to dichloroquinone led us to surmise that it did not differ greatly from it in constitution, so recourse was had to the use of aniline, which Niemeyer[6] had already used on the dichloroquinone. Niemeyer had found that the use of one equivalent of aniline led to the formation of 2,6-dichloro-5-anilinoquinone, together with 2,6-dichlorohydroquinone, while an excess replaced one chlorine atom with the formation of 2,5-dianilino-6-chloroquinone.

When our new quinone was treated in like manner, one equivalent of aniline introduced one anilino group without loss of chlorine, the hydroquinone being formed at the same time, giving 2-trichlorophenoxy-5-anilino-6-chloroquinone (IV) as the main product.

An excess of aniline, acting either on II or on its mono-anilino derivative, gave the same 2,5-dianilino-6-chloroquinone that Niemeyer had obtained from 2,6-dichloroquinone. This proved at once that the mono-anilino compound had the structure just indicated (2-trichlorophenoxy-5-anilino-6-chloroquinone IV since a second anilino group always enters *para* to one already present in a quinone ring. Trichlorophenol was isolated in fair amount from the reaction mixture showing that the second anilino group had replaced a trichlorophenoxy group.[7] This leads directly and unequivocally to Formula II for our new quinone, which may be distinguished briefly as the monophenoxyquinone.

In order to assure ourselves of the quinone nature of the anilino derivative IV, it was reduced to the hydroquinone, and this was acetylated to its triacetyl derivative. It was also possible to form a corresponding derivative with monomethylaniline in equivalent amount, this substance being blue; the mono-anilino derivative is red in crystalline form but blue in alkali.

2,6-Di-(2′,4′,6′-trichlorophenoxy)-*p*-benzoquinone III.—Quinone oxygen could not be determined in this substance, as it is too insoluble in hydrous solvents. Molecular-weight determinations were equally difficult on account of its low solubility, but a single determination gave a value (612) which indicated that it contained at least three benzene rings.

Its quinone nature was shown by reduction and acetylation of the product.

The action of an excess of aniline was tried, and it was found that a dianilino compound resulted, which still contained three chlorine atoms. The hydroquinone of III and trichlorophenol were easily isolated from the reaction mixture. It was considered that this was unequivocal evidence that the dianilino derivative must be 2,5-dianilino-6-trichlorophenoxy-

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[6] Niemeyer, *Ann.*, **228**, 335 (1885).

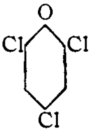
[7] This action is entirely in accord with the action of aniline on unsubstituted phenoxy groups attached to a quinoid ring. Compare Jackson and Grindley, *Proc. Am. Acad.*, **30**, 425 (1894).

quinone and hence the trinuclear oxidation product must have Structure III.

Mechanism of the Reaction

The formation of the mononuclear quinone I and of the dinuclear oxidation product, the phenoxyquinone II, are easily explained on the hypotheses used in the preceding paper. In the present work, the formation of the diphenoxyquinone III presents a problem which the present authors believe to be extremely difficult to explain on any other basis than that of the intermediate formation of doubly unsaturated radicals.

The explanation of this basis may be briefly stated as follows. The unsaturated radical V of Type A, if it loses chlorine spontaneously from the *para* position, will be oxidized to the dichloroquinone I. If it loses an *ortho* chlorine, it can then add another trichlorophenoxyl radical, to



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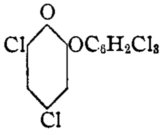

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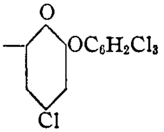

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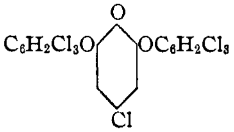

VIII

give VI, which then by loss of *para* chlorine and subsequent oxidation very easily gives II. If VI loses *ortho* chlorine to give VII, this may then add V again, giving VIII, which can give III by loss of chlorine and oxidation.

The formation of the diphenoxyquinone III is seen to be due to a further reaction of the same type which yields II. In the case of the tribromopyrogallol derivative, the radical corresponding to VI in the present paper did not yield a crystalline derivative corresponding to III. This may be explained as due to the superior stability of the chlorinated radical VII, which is able to unite with a free trichlorophenoxyl radical V in the presence of the slow oxidizing agent, lead dioxide in benzene.

This idea that the increase in number of nuclei is connected with the low velocity of oxidation, is borne out by the appearance, side by side with I, II and III, of an amorphous oxide in amount corresponding to about one-third of the original phenol, when the oxidizing agent is lead dioxide in benzene. This appearance seems to justify the original explanation of the formation of the oxides,[8] as due to the piling up of unsaturated radicals, and also to make it very probable that the polynuclear products obtained in the oxidation of the derivatives of pyrogallol and of trichlorophenol are in fact due to the oxidation of early stages in this polymerization process.

Further, only in a situation where the rate of oxidation is slow can the radicals find a continuous supply of the trichlorophenoxyl radical being

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[8] Hunter and Woollett, THIS JOURNAL, **43**, 135 (1921).

formed. An attempt is being made, to obtain further information on the relative velocities of the various reactions involved, in order that this most important point may be made entirely clear.

Experimental Part

A. Oxidation Experiments

Action of Nitrous Acid.—A solution of 2 g. of trichlorophenol in glacial acetic acid was treated with a current of oxides of nitrogen generated in a separate vessel by the acidification of sodium nitrite. The solution became yellow. When the gas current was allowed to flow for 24 hours, complete destruction of the phenol ensued. The addition of water produced an orange-brown color and gas was evolved. Evaporation of the solution caused the formation of white crystals, apparently of oxalic acid as they melted at 100°, and on further heating, solidified, to remelt at about 180°. About 0.3 g. was obtained from 2 g. of chlorinated phenol. When the action was stopped at different shorter intervals, various amounts of yellow precipitate could be obtained by the addition of water.

The use of sodium nitrite produced parallel results.

Action of Chromium Trioxide.—In this work the method of Kehrmann and Tiesler[3d] was used. To a solution of 25 g. of trichlorophenol in the minimum amount of glacial acetic acid prepared at 40–50° was added gradually a solution of 15 g. of chromium trioxide, dissolved in a little water and diluted with twice the volume of glacial acetic acid. The temperature was held at 30–40° by cooling and, after all of the chromium trioxide had been added, the mixture was allowed to stand for two hours. At the end of this time, 6 g. of long needles had separated, which were practically pure dichloroquinone I; yield, about 27%.

The filtrate was diluted with a large amount of water, whereupon 14 g. of yellow crystals slowly separated, which, when washed and dried, melted at 110–120°.

These contained dichloroquinone and the other oxidation product observed by Ling.[3e] His procedure was followed for their separation. Two g. of the yellow product was suspended in 20 cc. of water at 70°, and reduced with sulfur dioxide. Dark brown nodules appeared in place of the yellow material and were filtered off. The filtrate gave, on cooling, a precipitate of 0.4 g. of 2,6-dichlorohydroquinone melting at 150°.

The nodules were digested with alcohol. This left a light yellow residue, which melted at 132° after crystallization from glacial acetic acid; yield, 0.35 g. It was later shown to be 2-(2′,4′,6′-trichlorophenoxy)-6-chloro-*p*-benzoquinone II, which melts at 134–135° when pure.

Undoubtedly, the dark substance also observed by Ling was the quinhydrone of the above quinone and the 2,6-dichlorohydroquinone.

Action of Lead Dioxide in Glacial Acetic Acid.—Fifteen g. of trichlorophenol was dissolved in 150 cc. of glacial acetic acid. To the solution, cooled with ice water, was added all at once 18 g. of lead dioxide (equimolar amounts). This mixture was shaken, and filtered after an hour. Occasionally lead chloride continued to separate after this time, and in such cases the solution was allowed to stand until this action had ceased, and then refiltered. The slow addition of water produced a fine, yellow precipitate which was washed with 50% acetic acid, and air dried. Different samples at this point melted anywhere from 108° to 120°. The substance was then extracted twice with ether to remove small amounts of a red tar, and recrystallized from glacial acetic acid. It then melted at 122–125° and was later shown to be an impure monophenoxyquinone II.

The mother liquor, on addition of much water, yielded a lead salt, apparently of trichlorophenol, as this could be obtained from it. Evaporation of the aqueous acetic acid solution to dryness left a couple of grams of black tar which contained unchanged trichlorophenol.

Action of Lead Dioxide in Benzene.—Five g. of trichlorophenol was dissolved in 25 cc. of benzene, anhydrous sodium sulfate was added to remove water formed by the reaction, and finally 6 g. of lead dioxide was added all at once. The mixture was shaken frequently during an hour, and then filtered. The residue of lead compounds was washed with benzene, and the filtrate and washings were evaporated to dryness on the steam-bath.

After the benzene had evaporated, 2,6-dichloroquinone sublimed from the residue and was collected. The maximum obtained was 0.65 g., about 14% of the amount theoretically possible. Toward the end of the sublimation, higher-melting material usually appeared in small amount.

The red, tarry residue contained yellow crystals. Ether dissolved the tarry fraction and left a deep yellow, crystalline material, which melted at about 230° in the crude state, and usually weighed about 1 g., about 25% of the calculated amount. This later proved to be the 2,6-di-(trichlorophenoxy)quinone III, which melts at 245° when pure.

The ether solution of the tar was evaporated to dryness. The residue weighed 3.1 g. in one case. By repeated extraction of this residue with alcohol, hot and cold, a yield of about 1.6 g. of the monophenoxyquinone II was obtained from the alcohol or about 35% of the calculated amount.

The residual tarry material was amorphous. It dissolved in ether or chloroform with a red color and was precipitated by alcohol. It could not be brought to crystallization and presumably was related to the amorphous polyphenylene oxide obtained by the action of iodine on the sodium salt of trichlorophenol.[4] It was not investigated further.

B. Investigation of the Oxidation Products

I. 2,6-Dichloro-*p*-benzoquinone.—This substance has been reported as the sole result of the oxidation of *sym.*trichlorophenol by all the authors who have worked on the problem. It was obtained by us through repetition of the work of Kehrmann and Tiesler[3d] and of Ling.[3e]

It was also obtained by us as one of the products of oxidation of trichlorophenol, when treated with lead dioxide in dry benzene. On account of the difficulty experienced at first in distinguishing it from impure phenoxyquinone II, it was carefully studied, and comparison was made with a sample made by the oxidation of 2,6-dichloro-*p*-phenylenediamine. This left no doubt as to the identity of our material.

A sample was analyzed for quinonoid oxygen by titration with titanous chloride, and by the hydrazine method.

Anal. Calcd. for $C_6H_2Cl_2O_2$: quinonoid O, 18.02. Found: 18.15 ($TiCl_3$), 17.56 (N_2H_4).

II. 2(2′,4′,6′ - Trichlorophenoxy) - 6 - chloro - *p* - benzoquinone.—This substance is formed by oxidation of trichlorophenol in benzene with lead dioxide and in glacial acetic acid with chromium trioxide or with lead dioxide. Its isolation from these mixtures has already been described. Its purification and its recognition as a chemical entity were much complicated by its resemblance to 2,6-dichloroquinone in appearance, in the melting point of impure samples of it, and in their composition ($C_6H_2Cl_2O_2$) and ($C_{12}H_4Cl_4O_3$).

It was finally discovered that it could most easily be obtained in a very pure state by reducing it to the hydroquinone and reoxidizing this as described in the next section.

For experiments, the crude quinone was washed with ether and crystallized from glacial acetic acid until it melted at 125°. Material of this purity gave satisfactory analyses, and was considered sufficiently pure for use in preparation of other substances.

The pure quinone appears as pale yellow needles, often feathery, melting at 134–135°. It sublimes with difficulty. It is insoluble in cold ligroin, slightly soluble in cold alcohol, ether and glacial acetic acid, very soluble in the other ordinary solvents. It dissolves slowly in aqueous alkali, with deep-seated decomposition.

Anal. Calcd. for $C_{12}H_4O_3Cl_4$: C, 42.62; H, 1.19; Cl, 41.97; quinonoid oxygen, 9.46. Found: C, 43.14; H, 1.72; Cl, 42.11; quinonoid oxygen, 8.90, 9.51, 9.82 (by $TiCl_3$); 9.11 (by N_2H_4).

Mol. wt. Calcd. for $C_{12}H_4O_3Cl_4$, 338. Found (in benzene): 304, 346.

2-(2′,4′,6′-Trichlorophenoxy)-6-chlorohydroquinone.—The crude quinone was extracted with ether until free from tar, and then dissolved in acetone. Water was added until a slight permanent precipitate was formed, and then sulfur dioxide was passed into the solution for some time. The precipitate disappeared during this process, and when the reduction was complete, a little water did not cause any further precipitation in a small sample of the mixture. On evaporation in a current of air, white needles separated, which were twice recrystallized from chloroform. They then melted at 169° and were often slightly pink.

Anal. Calcd. for $C_{12}H_6O_3Cl_4$: Cl, 41.76. Found: 41.66.

Mol. wt. Calcd. for $C_{12}H_6O_3Cl_4$: 340. Found (in benzene): 329, 366.

Re-oxidation of the Hydroquinone.—This was easily accomplished by the addition of small quantities of lead dioxide to a glacial acetic acid solution of the hydroquinone until an excess of oxide was present, and then allowing the mixture to stand. The addition of water to the filtrate gave a precipitate of fine, yellow needles of the phenoxyquinone II, which melted at 134–135° after being washed and dried. Subsequent crops had a lower melting point.

Action of Aniline on Compound II

2-Trichlorophenoxy-5-anilino-6-chloro-*p*-benzoquinone.—To a hot solution of 8.3 g. of the phenoxyquinone II in 250 cc. of alcohol, prepared by heating on a steam-bath, were added 1.1 g. of aniline ($^1/_2$ molecular proportion) and 3.3 g. of concd. hydrochloric acid. The whole was heated for five minutes. On cooling, 2.3 g. of red needles separated. Concentration of the mother liquor gave a further less pure yield of 1.7 g.

The addition of water to the mother liquor gave a dark red oil. Extraction of this oil with cold chloroform left a solid residue, which proved to be the expected hydroquinone of Compound II.

The red crystals which formed the main product of the reaction were recrystallized, first from a large volume of alcohol and finally from equal parts of chloroform and alcohol by allowing the chloroform to evaporate in the cold; m. p., 194°. The compound is very soluble in chloroform, ether and benzene, and less so in alcohol. It is insoluble in aqueous alkalies but forms deep blue solutions with alcoholic solutions of alkalies.

Anal. Calcd. for $C_{16}H_9O_3Cl_4N$: N, 3.29; Cl, 33.06. Found: N, 3.81; Cl, 33.20.

Reduction Product.—A slight excess of stannous chloride dissolved in concd. hydrochloric acid was added to the alcoholic suspension of 1 g. of the anilino compound. The whole was heated for ten minutes on a steam-bath. The addition of water to the cooled solution caused the formation of a white precipitate, which crystallized on standing. The moist crystals turned pink rapidly in the air, so that it was necessary to dry them as rapidly as possible; yield, 0.4 g.; m. p., 156°. It was not possible to recrystallize this substance, even in the presence of sulfur dioxide, without contamination by oxidation products, so the first crop was analyzed after rapid drying.

Anal. Calcd. for $C_{18}H_{11}O_3Cl_4N$: Cl, 32.94. Found: 32.68.

Acetyl Derivative of the Reduction Product.—This was formed by refluxing the product just described for several hours with an excess of acetic anhydride. Purified by solution in alcohol and reprecipitation with water, it proved to be an amorphous powder, which could not be brought to crystallization. It was a triacetate.

Anal. Calcd. for $C_{24}H_{17}O_6Cl_4N$: Cl, 25.49. Found: 25.93.

2,5-Dianilino-6-chloro-*p*-benzoquinone.—This substance had already been obtained by Niemeyer[6] by the action of an excess of aniline on 2,6-dichloroquinone. It was very readily obtained from the phenoxyquinone II by the following procedure.

Five g. of the phenoxyquinone was dissolved in a large volume of boiling alcohol, and the solution treated with 3 g. of aniline. When heated on the steam-bath, the red solution turned brown, and brown, needle-like crystals separated. The cold mixture was filtered and the filtrate was evaporated for a second crop.

The solution now smelled strongly of trichlorophenol, so it was made alkaline and evaporated to dryness on the steam-bath. The residue was extracted with a little cold water. The filtered aqueous solution was acidified. The voluminous white precipitate proved to be trichlorophenol.

The main brown product was very insoluble in all solvents, as found by Niemeyer.

It was purified as far as possible by extraction with alcohol. It melted at 263°, as found by him and its identity was confirmed by analysis.

Anal. Calcd. for $C_{18}H_{13}O_2ClN$: Cl, 10.94. Found: 10.76.

Action of Monomethylaniline.—Two g. of the phenoxyquinone II was suspended in alcohol and treated with one-half of a molecular equivalent of monomethylaniline and hydrochloric acid, as described above for aniline. Dark blue needles separated on cooling and were crystallized from an alcohol-chloroform mixture; m. p., 164°. Analysis showed that the action was parallel to that of one-half equivalent of aniline. The substance is the *2-(trichlorophenoxy)-5-methylanilino-6-chloro-p-benzoquinone.*

Anal. Calcd. for $C_{19}H_{11}O_3Cl_4N$: Cl, 32.06. Found: 32.14.

III. 2,6-Di(2′,4′,6′-trichlorophenoxy)-*p*-benzoquinone.—As indicated under "Oxidation Experiments," this substance was obtained only by the oxidation of trichlorophenol by lead dioxide in dry benzene. It was easily purified by crystallization from benzene as deep yellow, warty crystals; m. p., 245°.

Anal. Calcd. for $C_{18}H_6O_4Cl_6$: C, 43.3; H, 1.21; Cl, 42.68. Found: C, 42.8; H, 1.37; Cl, 42.53.

Mol. wt. Calcd. for $C_{18}H_6O_4Cl_6$: 449. Found (Freezing point in benzene): 612. On account of the low solubility in cold organic solvents, a depression of only 0.045° was obtained.

Reduction of Compound III.—One g. of Compound III was dissolved and suspended in 25 cc. of glacial acetic acid on the steam-bath. To this hot solution was added a solution of stannous chloride in concd. hydrochloric acid, little by little, until the solution became colorless. The cold filtered solution gave a precipitate of fine, colorless needles on the addition of water. These melted at 235° after drying, and were already pure, as recrystallization from alcohol and water did not change the melting point; yield, almost quantitative.

Anal. Calcd. for $C_{18}H_8O_4Cl_6$: Cl, 42.51. Found: 42.30.

It was acetylated by heating with excess acetic anhydride for 15 hours.

ACETYL DERIVATIVE.—This was obtained as colorless needles from chloroform and alcohol, melting at 238°.

Anal. Calcd. for $C_{22}H_{12}O_6Cl_6$ (diacetate): Cl, 36.41. Found: 37.09, 37.11.

Action of Aniline on III.—Two g. of diphenoxyquinone III was heated on a steam-bath with 22 cc. of aniline until solution was complete. This required 24 hours. The excess of aniline was removed by solution in 25 cc. of glacial acetic acid and addition of water as long as precipitation continued. The brown, tarry precipitate was removed and extracted with cold glacial acetic, leaving a brown powder. This was crystallized from alcohol until it showed a constant melting point of 189°.

Trichlorophenol was again obtained from the mother liquor. However, the main product still contained chlorine and proved to have the expected composition, that of 2,5-dianilino-6-(2′,4′,6′-trichlorophenoxy)-*p*-benzoquinone.

Anal. Calcd. for $C_{24}H_{15}O_3N_2Cl_3$: Cl, 21.94. Found: 22.16.

Attempts at Synthesis of Compounds II and III

It was found that 2,6-dichloroquinone and trichlorophenol could not be brought to reaction in any way, in the time required for our oxidation experiments, even by heating together at the steam-bath temperature without a solvent. A very small yield (about 7%) of II was obtained by *several days'* heating of the dichloroquinone and trichlorophenol in benzene on the steam-bath but the time involved was so long that the result could have been due to oxidation by the air.

No way was found by which III could be formed either from I or II by the action of trichlorophenol.

Summary

1. The oxidation of *sym.*trichlorophenol yields not only 2,6-dichloroquinone as reported by previous investigators, but also a dinuclear product, 2-chloro-6-(2′,4′,6′-trichlorophenoxy)-*p*-benzoquinone, and a trinuclear product, 2,6-di-(2′,4′,6′-trichlorophenoxy)-*p*-benzoquinone.

2. The formation of these new products is interpreted as due to the intermediate formation of unsaturated radicals, of the general types $C_6H_2X_3O$- and —$C_6H_2Cl_2O$-.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

STUDIES ON THE DIRECTIVE INFLUENCE OF SUBSTITUENTS IN THE BENZENE RING. V. SOME SUGGESTED RELATIONS BETWEEN DIRECTIVE INFLUENCE AND THERMAL DATA[1]

BY A. W. FRANCIS, DONALD H. ANDREWS AND JOHN JOHNSTON

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The purpose of this paper is to point out some seeming parallelisms between the relative effect of the presence of a group in an aromatic compound upon its melting and boiling temperature and heat of melting, on the one hand, and the directive influence of the group, on the other. These parallelisms indicate that the directive influence is a permanent specific characteristic of the whole molecule rather than a temporary factor brought into play only at the moment of reaction through some "activation" process—an indication which is significant in connection with the mechanism of such reactions. In one sense this deduction is hardly novel, for it implies that the reactivity of certain classes of compounds is a function of structure just as melting temperature and heat of melting are; on the other hand, a connection between reactivity and structure would not at present be accepted as valid for all classes of compound and reaction, since it implies that catalysts would be without effect upon the relative order of the rates of reaction.

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[1] An elaboration of Part III of a dissertation presented by Alfred W. Francis in June, 1924, to the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy. It was presented in part at the sixty-ninth meeting of the American Chemical Society, Baltimore, April, 1925.