

LII.—*Studies on Isomeric Change.* No. IV. *Halogen Derivatives of Quinone.* Part I.

By ARTHUR R. LING.

THE following work, an account of which I have now the honour of presenting to the Chemical Society, had for its primary object the study of isomeric change, in extension of my previously-published observations on this phenomenon (Trans., 1887, **51**, 147 and 782; 1889, **55**, 583). During its progress, however, I have had occasion to examine all the known chloro-, bromo-, and chlorobromo-derivatives of quinone, and I can, for the most part, confirm the observations of other chemists as to their properties; in cases where this is not so, or in which I have improved the methods of preparing these derivatives, I have given my experiments in detail. Several new halogen derivatives of quinone will be described.

Paradichloroquinone.—This compound was prepared as described by Hantzsch and Schniter (*Ber.*, **20**, 2279) by treating quinone twice with concentrated (fuming) hydrochloric acid, and oxidising after each treatment. It may also be prepared by the following method, which, if it does not give quite as large a yield, has the advantage of being much more rapid:—Finely-pulverised quinol (50 grams) is suspended in concentrated hydrochloric acid (250 c.c.), specially prepared by saturating the ordinary concentrated acid with hydrogen chloride at 0°, and coarsely-pulverised potassium chlorate (37 grams, equivalent to 2 mols. of chlorine) is gradually added. Experiment has proved that the product is the same, whether the addition of the chlorate extends over one hour or eight hours; the temperature is kept at about 80°. The product is placed aside for about 12 hours, at the end of which time it has the appearance of a semi-solid, pulpy mass of crystals. The liquid portion is then drained off by means of the air-pump, and the crystals washed with cold water to remove potassium chloride, &c.; the paradichloroquinol which remains is almost pure, and, after crystallisation from boiling water, melts constantly at 172°. To obtain the quinone, the crude, moist quinol is suspended in dilute sulphuric acid, oxidised carefully with potassium dichromate, the product washed with water, dried, and finally washed with ether, when almost pure paradichloroquinone, weighing 25–30 grams and melting at 158–160°, remains; after crystallisation from alcohol, it melts at 161°. Analysis:—

0.3039 gram of substance gave 0.4941 gram AgCl.

	Calculated. $C_6H_2Cl_2O_2$.	Found.
Cl	40·11 per cent.	40·20 per cent.

The aqueous mother liquor and washings from the crude quinol contain, besides potassium chloride, monochloroquinol, which was identified by its melting point and that of the quinone obtained by oxidising it, and by analysis. Other compounds are present, and as a considerable amount of this bye-product has been collected from numerous experiments, I intend to make a complete examination of it.

Metadichloroquinone.—This compound is obtained in small quantity by adding trichlorophenol to nitric acid (sp. gr. 1·5), cooled in a freezing mixture of ice and salt, but the yield is augmented by the following modification:—Trichlorophenol (25 grams) is dissolved in alcohol (100 c.c.), the solution cooled in a freezing mixture of ice and salt, and nitric acid (sp. gr. 1·5) (50 grams), also cooled, gradually dropped in, the alcoholic solution being kept in agitation meanwhile; after about two hours, metadichloroquinone separates in yellow needles, and when crystallised from alcohol, weighs at most 10 grams, and melts at 121°. The alcoholic filtrate, when carefully added to water, yields a red, varnish-like substance, which becomes semi-solid after a time, and is free from nitrophenol, but attempts to isolate pure substances from it have hitherto been unsuccessful. The best method of preparing metadichloroquinone is that devised by Kehrmann and Tiesler (*J. pr. Chem.* [2], **40**, 480) by the action of chromic acid on trichlorophenol dissolved in glacial acetic acid. The product obtained by this method is free from resinous substances, but is not exclusively metadichloroquinone, as stated by Kehrmann and Tiesler; in the crude state it consists of yellow, microscopic needles, and melts at 115—120°. This is suspended in water (10 parts) at 70°, and after passing a current of sulphurous anhydride through the mixture for 10 minutes, the solution is filtered from the undissolved, black, nodular particles (see below), and the filtrate allowed to remain; metadichloroquinol separates after a while in colourless needles, of melting point 159—160°, and a further quantity may be obtained by evaporating the filtrate. After purification, metadichloroquinol melts at 164°, as stated by Kehrmann and Tiesler (*loc. cit.*). The above-mentioned black, nodular particles, when allowed to remain in contact with alcohol, break up, and the dark, superficial coating dissolves, leaving a yellow substance which melts at 117—120°; the latter, after being crystallised repeatedly from light petroleum, melts at about 125°, and has the form of small, yellow, feathery, felted needles, quite distinct from metadichloroquinone; it is now under investigation.

Diacetylmetadichloroquinone.—This compound has been described by Levy (*Ber.*, **16**, 1445), who records the melting point as 66.5° ; more recently, however, Kehrmann and Tiesler (*loc. cit.*) give 98° as the melting point. Metadichloroquinol dissolves in acetic anhydride with the evolution of heat, but only a small amount of the diacetyl derivative is formed. The whole of the quinol is converted into diacetyl derivative, however, when it is boiled in a reflux apparatus with acetic anhydride for about an hour. The product is extremely difficult to purify, and even after repeatedly evaporating with alcohol, it usually still contains acetic anhydride. A specimen, after crystallisation from dilute alcohol, was obtained in delicate needles and prisms, and melted at 76° . Analysis:—

0.145 gram of the substance gave 0.1604 gram AgCl.

	Calculated. $C_{10}H_8Cl_2O_4$.	Found.
Cl	26.99 per cent.	27.45 per cent.

I have since prepared another specimen which behaved as follows:—When the temperature was very slowly raised, it melted even as high as 111 – 113° , and resolidified at about 66° (Levy's temperature); whilst, if the temperature was quickly raised, it melted at 85 – 86° .

Metadichloroquinone is also obtained in small quantity by dropping diorthochloroparabromophenol into cooled nitric acid (see below). As the last-mentioned compound has not as yet been described, I will here give its method of preparation and characteristics.

Diorthochloroparabromophenol.—Sulphuryl chloride (40 grams) is added to fused parabromophenol (25 grams); the product is freed from acid, dissolved in sodium hydroxide solution, and reprecipitated with acid. After repeated crystallisation from dilute alcohol, it is obtained in silky needles, melts at 65° , and possesses a faint but penetrating odour. When recrystallised from light petroleum, it forms magnificent, long, silky needles, and melts constantly at 66.5° . Analysis:—

0.3116 gram of substance gave 0.6171 gram of mixed chloride and bromide of silver.

	Calculated. $C_6H_2Cl_2Br \cdot OH$.	Found.
Cl } Br }	62.39 per cent.	62.93 per cent.

When the dichlorobromophenol is dissolved in glacial acetic acid, and the solution heated with a slight excess of nitric acid (sp. gr. 1.42), it yields dichloroparanitrophenol (m. p. 125°) and orthochlororthoparadinitrophenol (m. p. 110 – 111°). Analyses of the potassium salts:—

I. 0.2243 gram of substance lost 0.0156 gram at 120°, and gave 0.0754 gram K_2SO_4 .

	Calculated. $C_6H_2Cl_2(NO_2)_2 \cdot OK + H_2O$.	Found.
H_2O	6.81 per cent.	6.95 per cent.
K	14.77 „	15.06 „

II. 0.2786 gram of substance lost 0.017 gram at 120°, and gave 0.0916 gram K_2SO_4 .

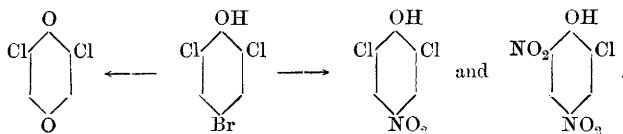
	Calculated. $C_6H_2Cl(NO_2)_2 \cdot OK + H_2O$.	Found.
H_2O	6.55 per cent.	6.10 per cent.
K	14.20 „	14.73 „

When the dichlorobromophenol (16 grams) is added to nitric acid (sp. gr. 1.5; about 70 grams) cooled in a freezing mixture of ice and salt, it yields a small quantity of metadichloroquinone; it is purified by crystallisation from alcohol, and melts at 121°, giving a quinol melting at 164°. Analysis:—

0.1671 gram of substance gave 0.2684 gram $AgCl$.

	Calculated. $C_6H_2Cl_2O_2$.	Found.
Cl	40.11 per cent.	39.73 per cent.

The above facts therefore establish the constitution of the dichlorobromophenol, thus:—



Metadibromoquinone.—This is obtained in small quantity, as stated by Levy and Schultz (*Annalen*, **210**, 158), by adding ordinary tribromophenol to cold nitric acid (sp. gr. 1.5). When pure, it forms golden-yellow leaflets, and melts at 131° (compare Heinichen, *Annalen*, **253**, 253). It is obtained in good yield by oxidising dibromoparamidophenol sulphate with a faintly acid solution of potassium chromate. The paramidophenol sulphate crystallises from dilute sulphuric acid in greyish needles. Analysis:—

I. 0.3557 gram of substance lost 0.0369 gram at 130°, and gave 0.122 gram $BaSO_4$.

II. 0.4296 gram of substance gave 0.1443 gram $BaSO_4$.

Calculated. [C ₆ H ₂ Br ₂ (NH ₂)·OH] ₂ ·H ₂ SO ₄ + 4H ₂ O.		Found.	
		I.	II.
H ₂ O....	10·22 per cent.	10·37	— per cent.
H ₂ SO ₄ ..	13·92 „	14·42	14·16 „

Metadibromoquinol is obtained by reducing the quinone with sulphurous acid; it forms long, (almost?) colourless leaflets, and melts at 163—164°. Analysis:—

0·4296 gram of substance gave 0·5984 gram AgBr.

	Calculated. C ₆ H ₂ Br ₂ (OH) ₂ .	Found.
Br	59·70 per cent.	59·26 per cent.

Metadibromoquinol is sparingly soluble in cold water or benzene, readily in the boiling liquids, and still more so in alcohol and glacial acetic acid; on oxidation, the quinone melting at 131° is obtained:—

Metachlorobromoquinone.—This compound is obtained in small yield when orthochlorororthoparadibromophenol (m. p. 76°); Garzino (*Atti. Real. Accad. Torino*, **25**; also *Ber.* **25**, Ref. 120), is added to nitric acid (sp. gr. 1·5) cooled by ice and salt. It crystallises from alcohol in yellow needles resembling metadihaloquinone, and melts at 114—115°. Nef (*Amer. Chem. J.*, **13**, 422) has recently prepared this compound and established its constitution. He states that it melts at 113°. 75 grams of orthochlorororthoparadibromophenol give 6 grams of pure metachlorobromoquinone; the remainder of the product being varnish-like substances, from which chlorobromoparanitrophenol (m. p. 137°; see *Trans.*, 1889, 57) and orthochlorororthoparadinitrophenol (m. p. 110—111°) were obtained, and identified by their melting points as well as by analyses of their barium and potassium derivatives.

Analysis of metachlorobromoquinone:—

0·2596 gram of substance gave 0·3876 gram of mixed chloride and bromide of silver.

	Calculated. C ₆ H ₂ ClBrO ₂ .	Found.
Cl } Br }	52·14 per cent.	52·00 per cent.

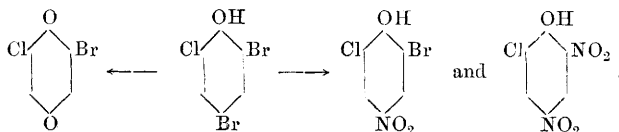
Metachlorobromoquinol is prepared by reducing the quinone with sulphurous acid; it resembles, in form and solubility, the corresponding dibromo-derivative, and melts at 154—155°. The following result was obtained on analysis:—

0·3362 gram of substance gave 0·4957 gram of mixed chloride and bromide of silver.

		Calculated.		Found.
		$C_6H_2ClBr(OH)_2$.		
Cl	}	51.67 per cent.		51.36 per cent.
Br				

The last-described quinol yields metachlorobromoquinone, melting at 114—115°, on oxidation. *Diacetylmetachlorobromoquinol* was not obtained in the pure state, as the same difficulties were encountered as mentioned above under the corresponding dichloro-derivative; it, however, appears to melt below 100°.

The relation of Garzino's chlorodibromophenol to metachlorobromoquinone and to the above-mentioned nitrophenol derivatives is shown by the following symbols:—



Paradichlorobromoquinone.

In a note read before the Chemical Society, March 6, 1890 (Proc., 1890, 32), I stated that when paradichloroquinone is brominated, paradichlorobromoquinone is obtained together with an isomeride, and I was led to this conclusion by certain observations made by Hantzsch which I have since proved to be incorrect. The product which I obtained apparently contained a small amount of chlorodibromoquinone, due to the presence of monochloroquinone in the crude paradichloroquinone employed (see above under paradichloroquinone). I separated pure paradichlorobromoquinone from this product, and the remaining portion which I believed to be an isomeride appears to have been a mixture of dichlorobromo- and chlorodibromoquinone, together with a small quantity of tetra-halogen derivative; this view is supported by the fact that the bromine determinations made with the supposed isomeric dichlorobromoquinone were too high. The presence of tetra-halogen derivative is accounted for as follows:—When the tri-halogen derivatives of quinone are repeatedly recrystallised from alcohol, they undergo partial decomposition, the solution becoming strongly acid. When an alcoholic solution of either of the halogen derivatives of quinone is evaporated, the residue consists almost entirely of resinous substances. It is thus probable that halogen is split off, and a certain amount of tetra-halogen derivative produced every time the tri-halogen derivatives are crystallised from alcohol. This tetra-halogen quinone is very much more stable, and at the same time much less soluble in alcohol, than the tri-derivatives,

and is therefore increased relatively in quantity each time the tri-derivatives are recrystallised from this solvent.

Paradichlorobromoquinone is obtained in good yield when paradichloroquinone is dissolved in glacial acetic acid, and bromine (1 mol. proportion) dropped into the solution. When the bromination is complete, which is usually the case after some hours, the solution is poured into water, the compound collected, washed, suspended in water (about 10 parts), and a current of sulphurous anhydride passed through at the ordinary temperature; it is then filtered from any unattacked tetra-halogen quinone which may be present (compare Graebe, *Annalen*, **263**, 16). The sulphurous anhydride is expelled from the filtrate by boiling, and after cooling and rendering acid with dilute sulphuric acid, an excess of potassium dichromate solution is cautiously added with agitation, and the precipitated paradichlorobromoquinone collected, washed, dried, and crystallised from alcohol. It forms thin, lustrous, yellow plates, resembling trichloroquinone, melts at 160—161°, and is readily soluble in boiling alcohol, but only sparingly in the cold; readily soluble in glacial acetic acid, benzene, and chloroform, but somewhat sparingly in boiling light petroleum. The following results were obtained on analysis:—

- I. 0.2329 gram of substance gave 0.4217 gram of mixed chloride and bromide of silver.
- II. 0.2198 gram of substance gave 0.4039 gram of mixed chloride and bromide of silver.

		Calculated.	Found.	
		$C_6HCl_2BrO_2$.	I.	II.
Cl }	58.98 per cent.		57.54	58.37 per cent.
Br }				

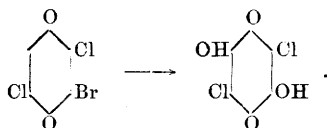
When paradichlorobromoquinone is heated with aqueous alkali, chloranilic acid is produced. The following result was obtained on analysing a specimen of air-dried chloranilic acid derived from the last-mentioned quinone:—

*0.0794 gram of substance gave 0.1026 gram AgCl.

		Calculated.	Found.
		$C_6Cl_2(OH)_2O_2 + H_2O$.	
Cl	31.27 per cent.		31.95 per cent.

* The above result was obtained with an exceedingly small weight of substance, a larger quantity not being available. The conclusion, as to the constitution of the dichlorobromoquinone, drawn from it, will, however, be found to be confirmed in a subsequent portion of the paper (see under paradichlorodibromoquinone). The chloranilic acid was characterised by its potassium salt.

This result establishes, therefore, the constitution of the dichloro-bromoquinone, thus :—



Pardichlorobromoquinol is obtained by reducing the quinone with sulphurous acid. It separates from its aqueous solution in small, lustrous prismatic needles containing 1 mol. H_2O , melts at $124\text{--}126^\circ$ when the temperature is raised slowly, partially resolidifies above this, and again melts at $134\text{--}135^\circ$. It loses its water of crystallisation at 70° , as the following determination shows :—

0.3552 gram of substance lost 0.0232 gram at 70° .

	Calculated.	Found.
	$\text{C}_6\text{HCl}_2\text{Br}(\text{OH})_2 + \text{H}_2\text{O}$.	
H_2O	6.52 per cent.	6.53 per cent.

The anhydrous compound crystallises from chloroform in small, felted needles, and melts at 133.5° ; it is readily soluble in boiling water, chloroform, and carbon bisulphide, sparingly in the cold liquids, and easily in alcohol.

The following results were obtained on analysis :—

- I. 0.127 gram of substance gave 0.236 gram of mixed chloride and bromide of silver, and this lost 0.0216 gram on ignition in a current of dry chlorine.
- II. 0.173 gram of substance gave 0.32 gram of mixed chloride and bromide of silver, and this lost 0.0305 gram on ignition in a current of dry chlorine.

	Calculated.	Found.	
	$\text{C}_6\text{HCl}_2\text{Br}(\text{OH})_2$.	I.	II.
Cl	27.51 per cent.	28.19	27.33 per cent.
Br	31.00 „	30.56	31.69 „

Diacetylparadichlorobromoquinol is prepared by boiling the quinol in a reflux apparatus for about an hour with acetic anhydride. It crystallises from boiling light petroleum in silky needles, and melts at $158\text{--}159^\circ$. Analysis :—

0.1883 gram of substance gave 0.2611 gram of mixed chloride and bromide of silver.

	Calculated.	Found.
	$\text{C}_6\text{HCl}_2\text{Br}(\text{OC}_2\text{H}_3\text{O})_2$.	
Cl }	44.15 per cent.	44.07 per cent.
Br }		

Paradichlorobromoquinol is also obtained together with paradichlorodibromoquinol when finely pulverised paradichloroquinone is boiled with concentrated fuming hydrobromic acid. These products were analysed and characterised, but it is unnecessary to give details.

Metadichlorobromoquinone is prepared in a similar manner to the para-derivative by treating metadichloroquinone dissolved in glacial acetic acid with bromine (1 mol. proportion). After crystallisation from boiling alcohol or light petroleum, it is obtained in thin, lustrous, yellow plates. It resembles the para-derivative in general form and solubility, and melts at 168° . In my former note (*Proc., loc. cit.*), I stated that this compound has not a sharp melting point, and I gave the value $175-180^{\circ}$. This is, however, erroneous, and the cause of the misstatement is that the quinone formerly described had been crystallised repeatedly from alcohol, and was contaminated with tetra-halogen derivative (see above under paradichlorobromoquinone). The following result was obtained on analysing a specimen of metadichlorobromoquinone:—

0.2224 gram of substance gave 0.4083 gram of mixed chloride and bromide of silver; this lost 0.0388 gram on ignition in a current of dry chlorine.

	Calculated. $C_6HCl_2BrO_2$.	Found.
Cl.	27.73 per cent.	27.17 per cent.
Br.	31.25 ,,	31.33 ,,

When metadichlorobromoquinone is heated with dilute alkali, chlorobromanilic acid is obtained. The potassium salt was analysed with the following result:—*

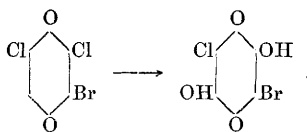
0.1332 gram of substance lost 0.0134 gram at 130° , and gave 0.0632 gram K_2SO_4 .

	Calculated. $C_6ClBr(OK)_2O_2 + 2H_2O$.	Found.
H_2O	9.84 per cent.	10.06 per cent.
K.	21.34 ,,	21.24 ,,

The constitution of metadichlorobromoquinone is therefore established by this result, thus:—

* A halogen determination was also made on the sodium salt.

	Calculated. $C_6ClBr(ONa)_2O_2 + 4H_2O$.	Found.
Cl.	9.60 per cent.	9.45 per cent.
Br.	21.65 ,,	20.13 ,,



Metadichlorobromoquinol is obtained by reducing the quinone with sulphurous acid; it is also formed together with paradichlorodibromoquinone (see below), when metadichloroquinone is boiled with concentrated fuming hydrobromic acid. It is, however, best prepared as follows:—Finely-pulverised metadichloroquinone (1 mol.) is suspended in dry carbon bisulphide or chloroform* (20 parts), and bromine (1 mol.) dropped in with agitation. After remaining for some hours with constant shaking, the liquid portion is removed, and the crude quinol spread upon a porous tile until the greater portion of the hydrogen bromide has passed off. It is generally pure after one crystallisation from boiling water or chloroform; it separates from either solvent in bunches of anhydrous, colourless needles, melts at 135° , and resembles the para-derivative as regards solubility. Analysis:—

0.1554 gram of substance gave 0.2842 gram of mixed chloride and bromide of silver, and this lost 0.0266 gram on ignition in a current of dry chlorine.

	Calculated. $C_6HCl_2Br(OH)_2$.	Found.
Cl	27.52 per cent.	27.28 per cent.
Br	31.00 ,,	30.75 ,,

Diacetylmetadichlorobromoquinone is prepared by boiling the quinol in a reflux apparatus with acetic anhydride. It crystallises from boiling benzene in colourless, microscopic needles, melts at 173 — 174° , and is readily soluble in chloroform, sparingly in cold alcohol and benzene, readily in the hot liquids; it is only sparingly soluble in boiling light petroleum, and almost insoluble in cold. Analysis gave the following result:—

0.2684 gram of substance gave 0.3681 gram of mixed chloride and bromide of silver, and this lost 0.0353 gram on ignition in a current of dry chlorine.

	Calculated. $C_6HCl_2Br(O \cdot C_2H_3O)_2$.	Found.
Cl	20.76 per cent.	20.19 per cent.
Br	23.39 ,,	23.61 ,,

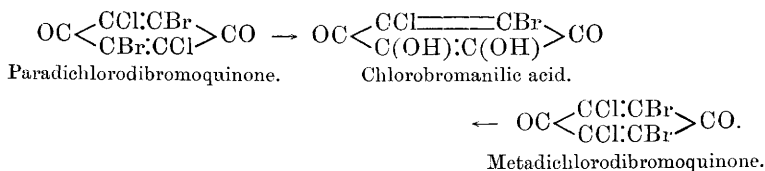
* When either of the dichloroquinols is treated with bromine in glacial acetic acid solution, oxidation accompanies bromination, and the quinone derivatives are obtained.

Tetrachloroquinone (chloranil) is conveniently prepared by passing a current of chlorine through the crude product of the action of potassium chlorate and hydrochloric acid on quinol (paradichloroquinol; see above) dissolved in glacial acetic acid, until it consists of a magma of yellow scales. The product is a mixture of tri- and tetra-chloroquinone, similar to that obtained from phenolsulphonic acid by Knapp and Schultz's method (*Annalen*, **210**, 175), and these are separated according to Graebe's latest directions (*Annalen*, **263**, 16), and crystallised from toluene. Pure tetrachloroquinone melts at 290°, as stated by Graebe (*loc. cit.*).

Tetrabromoquinone (bromanil) is obtained in almost theoretical yield when quinol (30 grams; 1 mol.) is dissolved in glacial acetic acid (300 c.c.), and bromine (4 mols.) run in with agitation. After adding all the bromine, the mixture is allowed to remain for some hours, a small quantity of nitric acid is then added, and it is heated on the water-bath for a short time to complete the bromination and oxidise any quinol derivative which may be present. When cool, it is poured into water, and the precipitated tetrabromoquinone collected, washed, dried, and crystallised from glacial acetic acid, and subsequently from benzene. The pure compound melts at 300°, as stated by Graebe and Welltner (*Annalen*, **263**, 31).

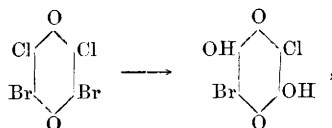
The remainder of my experiments deal with paradichlorodibromo- and metadichlorodibromo-quinone and their derivatives, and before describing them, it will be necessary to make some introductory remarks.

S. Levy stated (*Ber.*, **18**, 2366) that the so-called anilic acids were orthodihydroxy-derivatives of quinone, since he found that the same dihydroxychlorobromoquinone (chlorobromanilic acid) is obtained from both paradichlorodibromo- and metadichlorodibromo-quinone* on treating them with alkali; for example:—

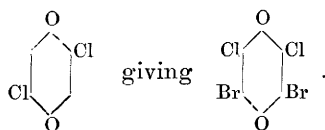


* Levy (*loc. cit.*) publishes crystallographic measurements of paradichlorodibromoquinone, and the corresponding quinol, made for him by T. Liweh (see also *Zeits. Kryst. Min.*, **11**, 246), and these indicate that the quinone is not isomorphous with metadichlorodibromoquinone (see Levy, *Ber.*, **16**, 1444), but that the two quinols are isomorphous. Mr. W. J. Pope has, however (see p. 573), recalculated Liweh's results, and found from his conclusion that paradichlorodibromoquinone is not isomorphous with the so-called metadichlorodibromoquinone is unsupported by the data.

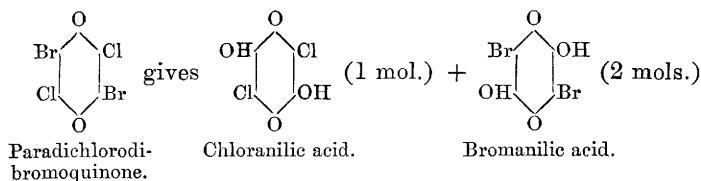
It was, however, subsequently proved by Hantzsch (*Ber.*, **19**, 2398) and by Nietzki (*ibid.*, 2727) that nitranilic acid, which is the analogue of chloranilic and bromanilic acids, is a paradihydroxy-derivative, thus, $\text{CO} < \begin{smallmatrix} \text{C}(\text{NO}_2):\text{C}(\text{OH}) \\ \text{C}(\text{OH}):\text{C}(\text{NO}_2) \end{smallmatrix} > \text{CO}$; and, finally, Hantzsch found (*Ber.*, **20**, 1303) that paradihydroxydibromoquinone, which he obtained by treating the basic sodium salt of paradihydroxyquinonedicarboxylic acid with bromine-water, is identical with bromanilic acid. It therefore became necessary to reconcile this result with those of Levy. Accordingly, Hantzsch and Schniter (*Ber.*, **20**, 2279) re-examined the two dichlorodibromoquinones from para- and meta-dichloroquinone, and also the corresponding quinols and their diacetyl derivatives, and finally arrived at the conclusion that the two sets of compounds from both sources were identical each to each. Inasmuch, therefore, as the dichlorodibromoquinone prepared from both para- and metadichloroquinone yielded, on treatment with alkali, chlorobromanilic acid, Hantzsch and Schniter concluded that it was metadichlorodibromoquinone,



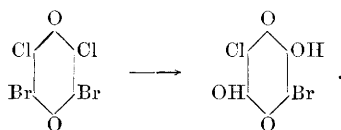
and that an isomeric change occurs when paradichloroquinone is brominated,



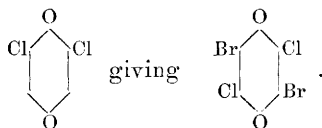
Previous to the appearance of Hantzsch and Schniter's paper, I had arrived at an identical conclusion, but withheld my views in order to investigate the subject more fully. This I have since done, and my experiments prove that the dichlorodibromoquinone obtained on brominating paradichloroquinone, at the ordinary temperature, and at the boiling point of glacial acetic acid, is a homogeneous compound, but that it does not give chlorobromanilic acid on treatment with alkali, as stated by Levy, and by Hantzsch and Schniter, but a molecular compound consisting of chloranilic acid (1 mol.) and bromanilic acid (2 mols.). There is, therefore, no reason for regarding this dichlorodibromoquinone as anything but the normal product, which will readily be seen on comparing the symbols:—



On studying the bromination of metadi-chloroquinone, I was surprised to find that the dichlorodibromoquinone obtained by brominating this at a high temperature also gave the same compound, consisting of chloranilic acid (1 mol.) and bromanilic acid (2 mols.) on treatment with alkali. Obviously, therefore, this could not be the normal product, metadi-chlorobromoquinone, which would give only chlorobromanilic acid, thus:—

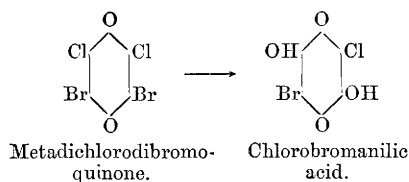


I can, therefore, confirm Hantzsch and Schniter's statement that the compound and its derivatives obtained by brominating paradi-chloroquinone are identical in all respects with those obtained by brominating metadi-chloroquinone when the experiments are conducted at a high temperature. An isomeric change must, however, be assumed to occur when metadi-chloroquinone is brominated under these circumstances,



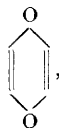
An extended study of the bromination products of metadi-chloroquinone at high and low temperatures, and that of metadi-chloroquinol, has completely confirmed this view, and my remaining results may thus be summed up:—When metadi-chloroquinone is brominated in glacial acetic acid solution at a temperature of 15—20°, a mixture consisting for the most part of the normal product, metadi-chlorodibromoquinone, together with a smaller quantity of paradi-chlorodibromoquinone, is obtained; whilst, if the reaction is performed at the boiling point of glacial acetic acid, paradi-chlorodibromoquinone is exclusively formed. Furthermore, when metadi-chlorobromoquinol (m. p. 135°) is suspended in an anhydrous menstruum and brominated, the normal product is produced, and this gives metadi-

chlorodibromoquinone on oxidation; the latter then yields chlorobromanilic acid on treatment with alkali, thus:—

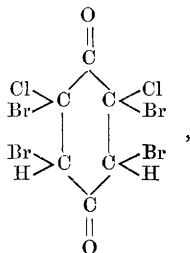


Mr. W. J. Pope, who has kindly furnished me with crystallographic measurements of several of the compounds described in this paper, finds that the last-mentioned dichlorodibromoquinone is crystallographically distinct from the isomeric para-derivative. The two compounds melt, however, within a degree of one another, and the melting points of their derivatives are very close; this is, however, not so surprising when it is remembered that all the tetra-halogen quinones and their derivatives are very close to one another in melting point. Mr. Pope also finds that paradichlorodibromoquinone, prepared from the two sources, gives measurements which are identical within the limits of experimental error.

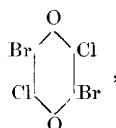
Representing quinone by Fittig's formula,



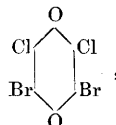
it cannot be strictly regarded as a benzene derivative, and an intramolecular redistribution of affinities must occur when it is reduced to quinol, a true benzene derivative. Nef has recently pointed out (*J. pr. Chem.* [2], **42**, 161) that quinone unites with 4 atoms of halogen to form derivatives of diketohexamethylene, and it thus appears probable that, whenever quinone is treated with halogen, the formation of an additive compound precedes that of a substitution derivative. It is conceivable, therefore, that when metadichloroquinone is treated with 2 mol. proportions of bromine, the dichloride-tetrabromide (dichlorotetrabromoparadiketohexamethylene),



is the primary product, and that this subsequently decomposes at a high temperature (that of boiling glacial acetic acid) into paradichlorodibromoquinone,



whilst, at the ordinary temperature, it decomposes for the most part into metadichlorodibromoquinone,



The production of paradichlorodibromoquinone requires the assumption of an intramolecular change, but such a change must also be assumed when quinone is converted into quinol. That such an intramolecular change would be likely to occur is, however, borne out by Nef's observation (*loc. cit.*) that quinone tetrabromide, on boiling with aqueous alcohol, yields a mixture of para- and meta-dibromoquinone. Before passing to the experimental portion, I will again draw attention to the fact that metadichloroquinol, when brominated at a temperature at which the corresponding quinone yields exclusively paradichlorodibromoquinone, gives the normal product. This is probably because the quinol is a true benzene derivative, and, therefore, as a saturated compound, direct substitution takes place.

Bromination of Paradichloroquinone.

Paradichlorodibromoquinone.—As already mentioned, Hantzsch and Schniter (*loc. cit.*) have put forward the view that when paradichloroquinone is brominated, metadichlorodibromoquinone is produced. This observation led me to study the bromination products of paradichloroquinone,* paradichloroquinol, and its diacetyl derivative, under various conditions, both at high and low temperatures; these experiments were made on an extensive scale, and the derivatives obtained were fractionally crystallised from every available solvent, the result being that they were found in all cases to be homogeneous substances and the normal products of the reactions. Several experiments were also made to determine the nature of the chlorination

* It may be added that the bromination of paradichloroquinone with both concentrated hydrobromic acid and bromine has been studied.

product of paradibromoquinone; in this case bromine is partially replaced by chlorine, and the products are probably chloranil, chlorotribromoquinone, and a dichlorodibromoquinone which was isolated and proved to be the para-derivative.

Paradichlorodibromoquinone is best prepared by dissolving paradichloroquinone (1 mol.) in glacial acetic acid (10 parts) at 70–80°, and dropping bromine (2 mols.) into the hot solution. After adding all the bromine, the crystalline magma is allowed to remain for a while, and then poured into an excess of water, collected, and washed. It is then suspended in water, and treated with potassium dichromate and dilute sulphuric acid, the object of this being to oxidise the tetra-halogen quinol which is invariably produced in small quantity; after this, it is again collected, washed, and dried; the yield is practically quantitative. It is crystallised first from glacial acetic acid, and subsequently from benzene. It forms six-sided plates, melts at 292°, and is sparingly soluble in glacial acetic acid at the ordinary temperature, more readily in the boiling liquid, and easily in boiling benzene; it is almost insoluble in cold alcohol, and only very slightly soluble in boiling. On adding light petroleum to its solution in benzene, it slowly separates out. The following result was obtained on analysing this compound:—

0·3824 gram of substance gave 0·7587 gram of mixed chloride and bromide of silver, and this lost 0·1004 gram on ignition in a current of dry chlorine.

	Calculated. $C_6Cl_2Br_2O_2$.	Found.
Cl.....	21·19 per cent.	21·63 per cent.
Br.....	47·76 „	47·19 „

Mr. W. J. Pope has measured some crystals of the above compound, and finds them to be identical in form with those of the so-called metadichlorodibromoquinone (Levy, *Ber.*, **16**, 1444); whereas, Liweh (*Zeit. Kryst. Min.* **11**, 247), as before stated, shows that the two compounds have different axial relations. Mr. Pope has, however, gone over Liweh's calculations and reports as follows:—"In this paper (*loc. cit.*), Liweh states that a comparison of the crystallographic elements of paradichlorodibromoquinone, $a : b : c = 1·446 : 1 : 2·850$; $\beta = 77^\circ 30'$ with those of metadichlorodibromoquinone, $a : b : c = 1·445 : 1 : 3·0286$; $\beta = 74^\circ 31'$ (Levy, *loc. cit.*), shows that these two compounds are not isomorphous, the ratio $a : b$ only remaining unaltered in the two substances, whilst the axis c is altered." "It can, however, be readily shown by readjusting the symbols allotted to the crystals of these two substances that the axial relations are practically the same in both." "Thus, starting from the para-compound $a : b : c$

$= 1.446 : 1 : 2.850$; $\beta = 77^\circ 30'$, by altering the symbols of the various forms, the axial relations $a : b : c = 1.4460 : 1 : 2.9025$; $\beta = 73^\circ 25'$ can be obtained, a set of values which are in fairly close agreement with those given by Liweh to the so-called metadichlorodibromoquinone." "The difference in the axial relations observed by Levy and Liweh is therefore only apparent, and this is confirmed by my own measurements, according to which the substances in question are crystallographically identical." "Any support which the crystallographic observations of Levy and Liweh have previously afforded to the view that the quinones from both sources are distinct compounds is thus rendered valueless."

When paradichlorodibromoquinone is heated with aqueous potassium or sodium hydroxide solutions (4—10 per cent.), it yields a compound consisting of chloranilic acid (1 mol.) and bromanilic acid (2 mols.), which cannot be separated into its constituents by crystallisation of either of its salts.

The sodium salt crystallises from water in massive, dark, almost black prisms which are red by transmitted light, belonging to the anorthic system, $a : b : c = 0.8825 : 1 : 0.8163$; $\alpha = 69^\circ 48'$; $\beta = 87^\circ 14'$; $\gamma = 72^\circ 11'$. Analysis:—

- I. 0.2224 gram of substance lost 0.0422 gram at 150° , and gave 0.0816 gram Na_2SO_4 .
- II. 0.2147 gram of substance lost 0.0403 gram at 150° , and gave 0.0779 gram Na_2SO_4 .
- III. 0.3171 gram of substance gave 0.2840 gram of mixed chloride and bromide of silver, and this lost 0.0489 gram on ignition in a current of dry chlorine.

	Calculated. $\text{C}_6\text{Cl}_2(\text{ONa})_2\text{O}_5, 2\text{C}_6\text{Br}_2(\text{ONa})_2\text{O}_2$ + $12\text{H}_2\text{O}$.	Found.			
		I.	II.	III.	
H_2O	18.65 per cent.	18.97	18.77	—	per cent.
Na	11.98 "	11.86	11.73	—	"
Cl	6.15 "	—	—	6.04	"
Br	27.75 "	—	—	27.71	"

The potassium salt crystallises in slender, dark-red needles. Analysis:—

- I. 0.2143 gram of substance lost 0.0205 gram at 150° , and gave 0.0959 gram K_2SO_4 .
- II. 0.1837 gram of substance lost 0.0169 gram at 150° , and gave 0.0825 gram K_2SO_4 .
- III. 0.2045 gram of substance gave 0.1855 gram of mixed chloride and bromide of silver, and this lost 0.0315 gram on ignition in a current of dry chlorine.

	Calculated.		Found.			
	$C_6Cl_2(OK)_2O_2 \cdot 2C_6Br_2(OK)_2O_2 + 6H_2O$		I.	II.	III.	
H ₂ O.....	9.46	per cent.	9.56	9.20	—	per cent.
K.....	20.50	„	20.05	20.11	—	„
Cl.....	6.22	„	—	—	6.35	„
Br.....	28.04	„	—	—	27.68	„

The dihydroxy-compound separates in brick-red scales on adding an excess of dilute hydrochloric acid to an aqueous solution of the alkali salts. The mean of two determinations obtained with a specimen of the substance dried at 120° gave the following values:—

	Calculated.	Found.
	$C_6Cl_2(OH)_2O_2 \cdot 2C_6Br_2(OH)_2O_2$	
Cl.....	8.81 per cent.	8.08 per cent.
Br.....	39.75 „	40.64 „

To prove that the last-described substance was really a compound of chloranilic acid (1 mol.) and bromanilic acid (2 mols.), sodium chloranilate and bromanilate were dissolved in water in this proportion. The crystals obtained were measured by Mr. Pope, and found to have the same axial relations as those above given by him for the salt from paradichlorodibromoquinone, thus:— $a : b : c = 0.8825 : 1 : 0.8143$; $\alpha = 69^\circ 56'$; $\beta = 87^\circ 7'$; $\gamma = 72^\circ 11'$. The axial relations of sodium chloranilate, bromanilate, and chlorobromanilate were also determined by Mr. Pope, thus:—Sodium chloranilate, $a : b : c = 0.8743 : 1 : ?$; $\alpha = 88^\circ 8'$; $\beta = 89^\circ 51'$; $\gamma = 72^\circ 30'$. Sodium bromanilate, $a : b : c = 0.8768 : 1 : 0.8100$; $\alpha = 69^\circ 28'$; $\beta = 87^\circ 56'$; $\gamma = 71^\circ 49'$. Sodium chlorobromanilate, $a : b : c = 0.888 : 1 : 0.814$; $\alpha = 69^\circ 59'$; $\beta = 87^\circ 3'$; $\gamma = 71^\circ 58'$. A comparison of the elements of the two samples of the salt $C_6Cl_2(ONa)_2O_2 \cdot 2C_6Br_2(ONa)_2O_2 + 12H_2O$, the one obtained from paradichlorodibromoquinone, and the other by mixing the constituents in the requisite proportions shows them to be crystallographically identical." "The differences between the axial relations of the various salts are small, but sufficiently great to characterise them as distinct compounds" (see also next paper). Analysis of the salt prepared by mixing sodium chloranilate (1 mol.) with sodium bromanilate (2 mols.), and crystallising the mixture from water:—

0.2921 gram of substance lost 0.0544 gram at 150°, and gave 0.1067 gram Na_2SO_4 .

	Calculated.	Found.
	$C_6Cl_2(ONa)_2O_2 \cdot 2C_6Br_2(ONa)_2O_2 + 12H_2O$	
H ₂ O.....	18.65 per cent.	18.62 per cent.
Na.....	11.98 „	11.83 „
		2 s 2

The dihydroxy-derivative obtained by decomposing the last sodium salt with acid gave, on analysis:—Cl, 7·44 per cent.; Br, 41·32 per cent. Calculated:—Cl, 8·81 per cent.; Br, 39·75 per cent.

When paradichlorodibromoquinol is reduced by Graebe's method (see *Annalen*, **263**, 16) with hydriodic acid and phosphorus, the corresponding quinol is obtained, crystallising from benzene in flat needles, and melting at 235—236°; it gives a diacetyl derivative, which crystallises from benzene or glacial acetic acid in needles, and melts at 269—270°; compare Hantzsch and Schniter (*loc. cit.*).

Bromination of Metadichloroquinone (high temp.).

Paradichlorodibromoquinone is also formed by brominating metadichloroquinone in boiling glacial acetic acid solution. The same quantity of glacial acetic acid is employed as given above for the bromination of the paradichloroquinone, and the experiment is conducted in the same manner as the latter, only at the boiling point of the solution. The dichlorodibromoquinone obtained in this way is in every respect identical with that obtained from paradichloroquinone, thus: it melts at 292°, yields a quinol melting at 235—236°, which gives a diacetyl derivative melting at 269—270°; and further, Mr. Pope has established the identity of the two compounds by crystallographic measurement (see above). The following result was obtained on analysing the quinone:—

0·2062 gram of substance gave 0·4023 gram of mixed chloride and bromide of silver, and this lost 0·0538 gram on ignition in a current of dry chlorine.

	Calculated. $C_6Cl_2Br_2O_2$.	Found.
Cl	21·19 per cent.	21·01 per cent.
Br	47·76 „	46·84 „

This quinone gives the compound of chloranilic acid (1 mol.) and bromanilic acid (2 mols.) on treatment with alkali.

Analysis of the sodium salt:—

- I. 0·3102 gram of substance lost 0·0568 gram at 150°, and gave 0·1144 gram Na_2SO_4 .
- II. 0·2109 gram of substance lost 0·0386 gram at 150°, and gave 0·0775 gram Na_2SO_4 .
- III. 0·5472 gram of substance gave 0·4899 gram of mixed chloride and bromide of silver, and this lost 0·0829 gram on ignition in a current of dry chlorine.

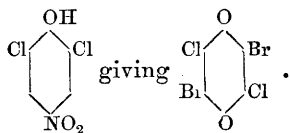
	Calculated. $C_6Cl_2(ONa)_2O_2, 2C_6Br_2(ONa)_2O_2$ + $12H_2O$.	Found.			
		I.	II.	III.	
H_2O	18.65 per cent.	18.31	18.30	—	per cent.
Na.....	11.98 „	11.94	11.90	—	„
Cl.....	6.15 „	—	—	6.31	„
Br.....	27.75 „	—	—	27.23	„

Potassium salt:—

0.226 gram of substance lost 0.0218 gram at 150° , and gave 0.1033 gram K_2SO_4 .

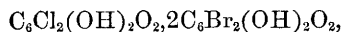
	Calculated. $C_6Cl_2(OK)_2O_2, 2C_6Br_2(OK)_2O_2$ + $6H_2O$.	Found.	
H_2O	9.46 per cent.	9.64	per cent.
K.....	20.50 „	20.49	„

I have previously described a compound as metadichlorodibromoquinone (Trans., 1887, 786), obtained by the action of bromine on dichloroparanitrophenol. I have carefully re-examined this, and find that it does not give chlorobromanilic acid on treatment with alkali, as stated (*loc. cit.*), but the molecular compound of chloranilic and bromanilic acids. The following values were obtained on analysing the sodium salt:— $H_2O = 18.41$ per cent.; $Na = 11.91$ per cent.; $Cl = 6.02$ per cent.; $Br = 28.13$ per cent. In the formation of this dichlorodibromoquinone, which must be the para-derivative, an isomeric change must occur, as shown by the following symbols:—



A dichlorodibromoquinone has been obtained by Kransse (*Ber.*, **12**, 47) by the action of bromine on dichloroquinonechlorimide. He shows that this quinone gives chlorobromanilic acid on treatment with alkali, and analyses of the potassium, sodium, and silver salts, as also of the acid itself, agreeing closely with the theoretical, are recorded; hence, the quinone must have been metadichlorodibromoquinone (compare above). Such a constitution is hardly conceivable, taking into account the source—dichloroquinonechlorimide—from which the quinone was derived, unless it were possible for the para-derivative to pass by isomeric change into the meta-compound. This, however, as shown above, is impossible, as the intramolecular change occurs in the reverse direction—the meta- into the para-derivative.

This being so, I can only conclude that the analyses recorded by Krause for chlorobromanilic acid and its salts are all wrong; that this chemist must have been dealing with the compound



and that the dichlorodibromoquinone must have been the para-derivative.

Bromination of Metadichlorobromoquinol.

Metadichlorodibromoquinone is readily obtained as follows:—*Meta*-dichlorobromoquinol (m. p. 135°), suspended in carbon tetrachloride (5 parts), is introduced into a strong stoppered bottle, and 1 mol. proportion of bromine, dissolved in carbon tetrachloride, is added. The stopper is then wired down and the bottle heated in a bath of boiling water for 5–6 hours. The liquid portion is decanted, and the product drained at the pump, and finally spread upon a porous tile until most of the hydrogen bromide, and all the carbon tetrachloride, is got rid of; it consists of crude *metadichlorodibromoquinol*, and usually melts at 220 – 225° . When repeatedly recrystallised from glacial acetic acid and benzene, it melts at 231 – 232° , and yields a diacetyl derivative melting at 265 – 266° .

It is mixed into a paste with water, and oxidised with potassium dichromate and dilute sulphuric acid. The crude quinone is then treated as described above, under the other tetra-halogen quinones, and finally crystallised from glacial acetic acid and benzene. It separates from benzene in six-sided plates, melts at 291° , and closely resembles the para-derivative, but is perhaps a little more soluble. "The crystals are probably monosymmetric, with the axial relations $a : b : c = 1.9654 : 1 : 0.6864$; $\beta = 90^\circ 0'$." "The substance is entirely distinct from the compound examined by Levy, to which he assigned the axial relations $a : b : c = 1.445 : 1 : 3.0286$; $\beta = 74^\circ 31'$." "The complete crystallographic investigation of the tetra-halogen quinones will be published later."

Analysis of *metadichlorodibromoquinone*:—

0.2156 gram of substance gave 0.4203 gram of mixed chloride and bromide of silver, and this lost 0.0572 gram on ignition in a current of dry chlorine.

	Calculated. $\text{C}_6\text{Cl}_2\text{Br}_2\text{O}_2$.	Found.
Cl.	21.19 per cent.	20.50 per cent.
Br.	47.76 ,,	47.77 ,,

Metadichlorodibromoquinone, when treated with alkali, gives chlorobromanilic acid. The sodium salt was obtained in dark,

almost black prisms, and crystallographic measurements have already been given for it (see above). Analysis:—

- I. 0.207 gram of substance lost 0.0402 gram at 150° and gave 0.0796 gram Na_2SO_4 .
- II. 0.3939 gram of substance gave 0.3521 gram of mixed chloride and bromide of silver, and this lost 0.0473 gram on ignition in a current of dry chlorine.
- III. 0.3987 gram of substance gave 0.3465 gram of mixed chloride and bromide of silver, and this lost 0.0469 gram on ignition in a current of dry chlorine.

	Calculated. $\text{C}_6\text{ClBr}(\text{ONa})_2\text{O}_2$ + $4\text{H}_2\text{O}$.	Found.			
		I.	II.	III.	
H_2O	19.48 per cent.	19.42	—	—	per cent.
Na.....	12.44 „	12.41	—	—	„
Cl.....	9.60 „	—	9.56	9.26	„
Br.....	21.65 „	—	21.58	21.14	„

The salts of chlorobromanilic acid are much less stable than those of the other anilic acids; they decompose when their aqueous solutions are boiled for a long time, the latter becoming acid; it is therefore necessary, in recrystallising these salts, to previously render the solvent water slightly alkaline.

The potassium salt crystallises in slender, reddish-brown needles. Analysis:—

0.184 gram of substance lost 0.0188 gram at 150°, and gave 0.0879 gram K_2SO_4 .

	Calculated. $\text{C}_6\text{ClBr}(\text{OK})_2\text{O}_2 + 2\text{H}_2\text{O}$	Found.
H_2O	9.84 per cent.	10.21 per cent.
K.....	21.34 „	21.35 „

Chlorobromanilic acid separates on adding an excess of dilute hydrochloric acid to either of its alkali salts in brick-red, flat needles.

Metadichlorodibromoquinol is obtained by reducing the quinone with hydriodic acid and phosphorus. It crystallises from glacial acetic acid or benzene in colourless needles, and, when pure, melts at 231—232°. It is readily soluble in alcohol, but is precipitated from this solvent on the addition of water; it is sparingly soluble in boiling glacial acetic acid, even less so in boiling benzene, very sparingly in boiling water, and practically insoluble in the cold. Analysis:—

0.5628 gram of substance gave 1.1019 gram of mixed chloride and bromide of silver.

		Calculated. $C_6Cl_2Br_2(OH)_2$.	Found.
Cl }	68.54 per cent.	68.21 per cent.	
Br }			

Diacetylmetadichlorodibromoquinol.—This is prepared by boiling the last-described quinol in a reflux apparatus with acetic anhydride. After crystallisation from glacial acetic acid or benzene, it is obtained in small, colourless needles, and melts at 265—266°. It is very sparingly soluble in glacial acetic acid and benzene at the ordinary temperature, and not very soluble in the boiling liquids. Analysis:—

0.3276 gram of substance gave 0.5079 gram of mixed chloride and bromide of silver.

		Calculated. $C_{10}H_6Cl_2Br_2O_4$.	Found.
Cl }	54.86 per cent.	54.01 per cent.	
Br }			

Bromination of Metadichloroquinone (low temp.).

When metadichloroquinone (1 mol.) is dissolved in glacial acetic acid (10 parts) and treated with bromine (2 mols.) at a temperature of 15—20°, metadichlorodibromoquinone, mixed with a smaller quantity of paradichlorodibromoquinone, is obtained. The product crystallises from benzene in six-sided plates, and melts at about 292°. Analysis:—

0.2731 gram of substance gave 0.5395 gram of mixed chloride and bromide of silver, and this lost 0.0721 gram on ignition in a current of dry chlorine.

		Calculated $C_6Cl_2Br_2O_2$.	Found.
Cl.	21.19 per cent.	21.23 per cent.	
Br	47.76 ,,	47.41 ,,	

On decomposing this quinone with sodium hydroxide solution, a salt was obtained, crystallising in dark prisms, and giving numbers on analysis agreeing fairly well with those required for sodium chlorobromanilate, thus:—

- I. 0.3725 gram of substance lost 0.0709 gram at 150°, and gave 0.1409 gram Na_2SO_4 .
- II. 0.268 gram of substance lost 0.0515 gram at 150°, and gave 0.1004 gram Na_2SO_4 .
- III. 0.2519 gram of substance gave 0.2265 gram of mixed chloride and bromide of silver, and this lost 0.0323 on ignition in a current of dry chlorine.

	Calculated. $C_6ClBr(O_2Na)_2O_2$ + $4H_2O$.	Found.			
		I.	II.	III.	
H_2O	19.48 per cent.	19.03	19.21	—	per cent.
Na.....	12.44 „	12.25	12.13	—	„
Cl.....	9.60 „	—	—	8.81	„
Br.....	21.65 „	—	—	23.06	„

These numbers do not exhibit as close an agreement with the theoretical as usual, although the utmost care was taken with the various determinations. As before mentioned, the dichlorodibromoquinone, from which the salt was obtained, is a mixture, and consequently the salt must also be a mixture. That the dichlorodibromoquinone is a mixture, is seen by the following experiments:—A portion of the quinone was reduced with hydriodic acid and phosphorus, and the quinol repeatedly crystallised from glacial acetic acid, when a small quantity of a compound melting at 235° (the melting point of paradichlorodibromoquinol) was obtained; whilst, on adding water to the united glacial acetic acid mother liquors, a compound was precipitated which melted at 231° (the melting point of metadichlorodibromoquinol). The former gave a diacetyl derivative melting at 268 — 269° , and the latter, a similar derivative melting at 265 — 266° . By fractionally crystallising the dichlorodibromoquinone from benzene, it was resolved into two portions, which gave quinols and diacetyl derivatives exhibiting the same differences in melting point as the last-mentioned. As these experiments were made with fairly large quantities of material, and taking into account the fact that metadichloroquinone yields, exclusively, paradichlorodibromoquinone on brominating it at a high temperature, the inference that the bromination product of metadichloroquinone at a temperature of 15 — 20° also contains a small quantity of paradichlorodibromoquinone appears to be justified. This work was suggested to me some years ago by Dr. H. E. Armstrong, to whom my best thanks are due.