LXXIX.—*Isomeric Change in the Phenol Series.* (Second Notice.)

By ARTHUR R. LING.

IN extending the experiments recorded in my previous communication on "The Action of Bromine on the Dibromonitrophenols" (this vol., p. 147), to some other nitro-halogen-derivatives of phenol, I have obtained results which are, I think, sufficiently interesting for publication.

II. *The Action of Bromine on the Dichloronitrophenols.*

1. *Dichlorororthonitrophenol*.—This compound was prepared in two ways, viz., by chlorinating orthonitrophenol, and by nitrating crude dichlorophenol, the product in each case being purified by means of the potassium salt, which crystallises from water in anhydrous flat red needles or plates. The following result of a potassium determination shows that the substance was pure:—

0·3148 gram dried at 100° gave 0·1130 gram K_2SO_4 .

	Theory.	Found.
	$C_6H_2Cl_2NO_3K$.	
K.	15·87 per cent.	15·75 per cent.

On treatment with dilute hydrochloric acid, this salt yielded dichlorororthonitrophenol, crystallising from alcohol in light yellow plates melting at 123°, the recorded melting point. 10 grams of dichlorororthonitrophenol was placed in a bottle together with one molecular proportion of bromine (8 grams), and about 40 c.c. of water; the stopper being fastened down with copper wire, the bottle was heated in a bath of boiling water for several hours. The bromine was entirely absorbed, and oxides of nitrogen escaped on releasing the stopper. The product was washed with water, dried and boiled with alcohol

which dissolved the greater portion. The residue was found to consist of a substance which dissolved but sparingly in alcohol, was insoluble in potassium carbonate solution, and did not contain nitrogen. In a second experiment similarly conducted, after a preliminary exhaustion with alcohol, the residue was dried and treated with benzene, in which it was found to be easily soluble, and to be deposited from the hot solution in glistening yellow plates, much resembling bromanil in appearance. A further qualitative examination showed that it contained both chlorine and bromine.

The portion dissolved by alcohol in the two foregoing experiments consisted of unaltered dichloronitro-compound. It seemed desirable, however, to obtain a larger quantity of the chlorobromo-derivative before investigating any other products of the reaction.

Since the reaction between dichlororthonitrophenol and bromine appeared somewhat analogous to that between dibromorthonitrophenol and bromine, it was probable that the unknown compound was a tetra-substitution-derivative of quinone, and if such were the case, it might be, assuming the parachlorine-atom in dichlororthonitrophenol, after its first displacement, to be rendered active by the nitric acid resulting from the displacement of the NO_2 -group, a dichlorodibromoquinone, two of which are known; or, if otherwise it might be chlorotribromoquinone, a hitherto unknown compound. Analysis has shown it to be the latter.

Chlorotribromoquinone.—In order to prepare this compound in larger quantity, several quantities of 5 grams of dichlororthonitrophenol were heated as before described with bromine in the proportion $\text{C}_6\text{H}_3\text{Cl}_2\text{NO}_3 : 4\text{Br}_2$ and water. The reaction takes place so readily that chlorotribromoquinone may be prepared by merely heating the dichloronitro-compound on the water-bath with bromine and water, in a flask connected with a reflux condenser. After the usual preliminary purification, the compound was crystallised from benzene. A certain portion was recrystallised from glacial acetic acid.

The numbers obtained on analysis were as follows:—

I.	0.1983 gram dried at 100°	gave 0.1405 gram CO_2 .
II.	0.2067	„ „ 0.3860 „ $\text{AgCl}(\text{AgBr})_3$.
III.	0.3392	„ „ 0.6328 „ $\text{AgCl}(\text{AgBr})_3$.

Theory.		Found.			
		I.	II.	III.	
$\text{C}_6\text{ClBr}_3\text{O}_2$.					
C	18.97 per cent.	19.31	—	—	per cent.
*Cl . . . }	72.59 „	—	72.85	72.78	„
Br . . . }					

* So many halogen determinations have been made of this compound and its

The equation showing the formation of chlorotribromoquinone from dichlororthonitrophenol and bromine is therefore—

Chlorotribromoquinol.—5 grams chlorotribromoquinone was introduced into a flask together with a solution of stannous chloride; the flask was connected with a reflux condenser, and the solution boiled on a sand-bath for about 20 minutes. The substance had then lost its yellow colour. It was thrown on to a filter, washed with water, and crystallised from benzene, from which it separated in colourless needles. After recrystallisation, the melting point was found to be 234° .

A specimen dried at 100° gave the following result on analysis:—

0.2920 gram gave 0.5411 $\text{AgCl}(\text{AgBr})_3$.

Theory.		Found.
$\text{C}_6\text{ClBr}_3(\text{OH})_2$.		
$\left. \begin{array}{l} \text{Cl} \\ \text{Br} \end{array} \right\} \dots\dots\dots$	72.21 per cent.	72.26 per cent.

Diacetylchlorotribromoquinol.—To prepare this compound, 2 grams chlorotribromoquinol was boiled with acetic anhydride for about two hours in a flask attached to a reflux condenser. It crystallises from benzene in colourless microscopic prisms, melting at 262° .

0.1950 gram dried at 100° gave 0.2953 gram $\text{AgCl}(\text{AgBr})_3$.

Theory.		Found.
$\text{C}_{10}\text{H}_4\text{ClBr}_3\text{O}_4$.		
$\left. \begin{array}{l} \text{Cl} \\ \text{Br} \end{array} \right\} \dots\dots\dots$	59.18 per cent.	59.08 per cent.

Chlorobromanilic Acid.—When chlorotribromoquinone is treated with potash according to Stenhouse's method, the potassium salt of chlorobromanilic acid (dihydroxychlorobromoquinone) is obtained. On adding an acid to an aqueous solution of the salt, the hydroxy-derivative is obtained. Chlorobromanilic acid was first described by Krause (*Ber.*, 12, 47), who prepared its potassium salt by the action of potash on metadichlorometadibromoquinone.

It is not at all easy to decompose chlorotribromoquinone with potash at the ordinary temperature; for example, 5 grams was not entirely decomposed in a week, although the flask containing the mixture was shaken vigorously at intervals during each day. If,

derivatives, and the numbers so closely approximate those demanded by theory, that I did not separate the chlorine and bromine. The silver precipitate has, however, in each experiment been qualitatively examined.

however, the solution be heated to boiling, the transformation takes place at once, but the yield is very considerably diminished. It has been found best to perform this experiment at 70—80°; the reaction is then complete in about six hours if 5 grams of substance be used. In no case is anything like the theoretical yield obtained; the largest quantity of the pure chlorobromanilic acid obtained from 5 grams of chlorotribromoquinone was under 1 gram.

A specimen recrystallised from water, and dried at 100°, was analysed with the following result:—

0.1962 gram gave 0.2541 gram $\text{AgCl}(\text{AgBr})_3$.

Theory.		Found.
$\text{C}_6\text{ClBrH}_2\text{O}_4$.		
Cl }	45.56 per cent.	45.21 per cent.
Br }		

Potassium Chlorobromanilate.—Some of the chlorobromanilic acid was converted into the potassium salt by means of potassium carbonate. The resulting salt recrystallised from water and dried between filter-paper was then analysed.

I. 0.2259 gram lost 0.0227 gram at 100—120°.

II. 0.3537 gram gave 0.1849 gram K_2SO_4 .

Theory.		Found.	
$\text{C}_6\text{ClBrK}_2\text{O}_4, 2\text{OH}_2$.		I.	II.
H_2O	9.84 per cent.	10.04	— per cent.
K	21.34 „	—	21.45 „

0.2007 gram anhydrous salt gave 0.1063 gram K_2SO_4 .

Theory.		Found.
$\text{C}_6\text{ClBrK}_2\text{O}_4$.		
K	23.67 per cent.	23.71 per cent.

Several experiments were made in order to ascertain whether, when dichlororthonitrophenol is heated with water and an insufficient quantity of bromine to entirely convert it into chlorotribromoquinone, the residual dichloronitro-compound undergoes isomeric transformation or any other change, the quantities used being 10 grams of dichlororthonitrophenol to 1 molecular proportion bromine and about 40 c.c. water. The heating was continued for several days, and the products, after washing, were boiled with potassium carbonate solution. The quinone-derivative was, in each case, decomposed by this treatment. In one instance, it appeared as a black carbonaceous mass, and in all the others as an amorphous, earth-coloured powder, which dissolved easily in benzene, but from which nothing definite could be obtained.

The action of alkalis, and more especially of carbonated alkalis, on

tetra-halogen-derivatives of quinone is, in my opinion, worthy of attention. Stenhouse mentions, in describing the preparation of chloranilic acid from chloranil (*Jour. Chem. Soc.*, 1870, 6), that, although potassium chloranilate was produced by the action of potassium carbonate on chloranil, a much better yield was obtained when caustic potash was used.

The alkaline extract from these experiments was found to consist of the potassium-derivative of dichlorororthonitrophenol, and hence it may be satisfactorily concluded that this compound undergoes no change when treated in the manner above mentioned. A specimen of the salt was recrystallised and analysed.

0.1503 gram dried at 100° gave 0.0529 gram K_2SO_4 .

	Theory. $C_6H_2Cl_2NO_3K$.	Found.
K	15.87 per cent.	15.76 per cent.

A portion treated with dilute hydrochloric acid and crystallised from alcohol was found to melt at 123°.

2. *Dichloroparanitrophenol*.—This was prepared by chlorinating paranitrophenol and purified by means of the potassium or barium salt. A barium salt has been obtained which agrees in appearance with one described in the text-books as crystallising in red needles containing 4 mols. H_2O . The salt obtained, however, apparently only contains $3\frac{1}{2}$ mols. H_2O . The following is the result of analysis:—

0.2838 gram lost 0.0290 gram at 100—120° and gave 0.1077 gram $BaSO_4$.

	Theory. $(C_6H_2Cl_2NO_3)_2Ba, 3\frac{1}{2}H_2O$.	Found.
H_2O	10.26 per cent.	10.21 per cent.
Ba.	22.31 „	22.31 „

10 grams of dichloroparanitrophenol was heated in the usual manner with bromine and water, the proportions used being

The product was crystallised from glacial acetic acid, and had the general form of the tetra-halogen-derivatives of quinone, viz., golden-yellow laminæ. A specimen dried at 100° was then analysed.

0.1916 gram gave 0.3787 gram of a mixture of $AgCl$ and $AgBr$, which on complete reduction gave 0.2469 gram metallic silver = 0.1662 gram $AgCl$ and 0.2125 gram $AgBr$.

	Theory. $C_6Cl_2Br_2O_2$.	Found.
Cl	21.19 per cent.	21.50 per cent.
Br	47.76 „	47.29 „

The compound was therefore a dichlorodibromoquinone, and as it was obtained from dichloroparanitrophenol, it must be the meta-dichlorometadibromoquinone described by Krause (*Ber.*, **12**, 47).

2 grams metadichlorometadibromoquinone was treated with potash in the usual manner. The salt obtained, after purification, was dried between filter-paper and analysed.

0.2464 gram lost 0.0247 gram at 100—120° and gave 0.1157 gram K_2SO_4 .

	Theory. $C_6Cl_2BrK_2O_4 \cdot 2OH_2$.	Found.
H_2O	9.84 per cent.	9.97 per cent.
K	21.34 „	21.02 „

The salt was therefore potassium chlorobromanilate, which, as before stated, has been previously obtained by Krause (*loc. cit.*) from meta-dichlorometadibromoquinone.

It is noteworthy that the decomposition of metadichlorometadibromoquinone by potash is effected with much greater ease than that of chlorotribromoquinone.

The production of metadichlorometadibromoquinone from dichloroparanitrophenol and bromine is represented by the following equation:—

III. Action of Bromine on Parachlororthonitrophenol.

Parachlororthonitrophenol was prepared both by chlorinating ortho-nitrophenol and by nitrating parachlorophenol. It was purified by means of its sodium salt, which crystallises from water in red prisms of the formula $C_6H_3ClNO_3Na \cdot H_2O$. On treating this with dilute hydrochloric acid, and crystallising the resulting compound from alcohol, parachlororthonitrophenol was obtained in large, yellow prisms melting at 87°. The recorded melting point is 86—87°.

A known weight of parachlororthonitrophenol was dissolved in glacial acetic acid and treated with one molecular proportion of bromine, the solution being kept cool. After separating the product in the usual manner, it was dissolved in boiling alcohol, from which it was deposited on cooling in large, sulphur-yellow scales melting sharply at 125°. A portion converted into the potassium salt, decomposed with dilute acid and crystallised from alcohol, was found to melt at the same temperature.

If the above compound were a normal bromination product of parachlororthonitrophenol, it would be parachlororthobromorthonitrophenol, and would give bromanil on treatment with bromine and

water at 100° , the parachlorine-atom being displaced by one of the oxygen-atoms in the quinone, just as it is in the case of orthopara-dichlororthonitrophenol (*vide ante*).

2 grams of supposed parachlororthobromorthonitrophenol was therefore heated with four molecular proportions of bromine and water in the usual way. It was entirely converted into a compound insoluble in alcohol and in potassium carbonate solution, containing bromine but no chlorine. In the solution filtered from the crude substance, however, hydrogen chloride as well as hydrogen bromide was detected. It was crystallised from benzene, dried at 100° , and analysed.

0.2839 gram gave 0.5029 gram AgBr.

	Theory. $C_6Br_4O_2$.	Found.
Br	75.47 per cent.	75.52 per cent.

The production of bromanil from this nitro-halogen-derivative affords conclusive evidence that it is parachlororthobromorthonitrophenol.

Potassium Parachlororthobromorthonitrophenol.—This compound crystallises in beautiful, dark-red, anhydrous needles, sparingly soluble in cold water. Analysis:—

0.1807 gram dried at 100° gave 0.0540 gram K_2SO_4 .

	Theory. $C_6H_2ClBrNO_3K$.	Found.
K	13.42 per cent.	13.39 per cent.

Barium Parachlororthobromorthonitrophenol.—This is not at all a characteristic compound. It is obtained as an orange-yellow precipitate when barium chloride is added to a solution of the potassium salt, also by boiling the phenol with water and barium carbonate. It is only slightly soluble in boiling water, and nearly insoluble in the cold. It is deposited from its solution in boiling water in tufts of orange-yellow needles, resembling in appearance the barium salt of dichlororthonitrophenol, which has the composition $C_6H_2Cl_2NO_3K, 2H_2O$. Unlike the crystals of the last-mentioned compound, these needles appear to lose their form on separating them from the mother-liquor. They, however, then contain 1 mol. H_2O . Analysis gave the following numbers:—

- I. 0.1427 gram lost 0.0040 gram at $100-120^{\circ}$ and gave 0.0503 gram $BaSO_4$.
- II. 0.1647 gram gave 0.0591 gram $BaSO_4$.

Theory.		Found.	
$(C_6H_2ClBrNO_3)_2Ba.H_2O.$		I.	II.
H ₂ O	2.70 per cent.	2.80	— per cent.
Ba.	20.82 „	20.74	21.06 „

The anhydrous salt is much darker in colour than the hydrated.

Calcium Parachlororthobromorthonitrophenol.—This forms orange-red, glistening scales, very slightly soluble in cold water. Dried between filter-paper, they gave the following result on analysis :—

0.2140 gram lost 0.0177 gram at 100–120° and gave 0.0531 CaSO₄.

Theory.		Found.
$(C_6H_2ClBrNO_3)_2Ca.2\frac{1}{2}H_2O.$		
H ₂ O	8.21 per cent.	8.31 per cent.
Ca	7.17 „	7.28 „

At this stage of my experiments, I learnt from Dr. Armstrong that a chlorobromonitrophenol had lately been obtained in his laboratory by the action of bromine and water at 100° on parachlorodithonitrophenol, m. p. 80.5°. From the manner in which it was produced, this compound ought to be identical with the one just described, but from the appearance of the potassium-derivative, which was in red scales, such did not seem to be the case. It seemed probable, therefore, that at the moment of substituting bromine for nitroxyl, isomeric change had taken place. The following experiments were made in order to investigate this matter.

10 grams of parachlororthonitrophenol, m. p. 87°, was dissolved in acetic acid and the solution boiled with one molecular proportion of bromine for half an hour in a flask attached to a reflux condenser. It was then left to cool for some hours, separated in the usual way, and crystallised from alcohol, from which it separated in yellow prisms melting at 120°. A portion was converted into the potassium salt, which was obtained in red anhydrous plates, agreeing with Dr. Armstrong's description. A specimen of this salt dried at 100° was then analysed :—

0.1639 gram gave 0.0500 gram K₂SO₄.

Theory.		Found.
$C_6H_2ClBrNO_3K.$		
K	13.42 per cent.	13.66 per cent.

It is thus seen that the compound obtained by brominating parachlororthonitrophenol at a temperature near to 100° is isomeric and not identical with that obtained by performing the same experiment at the ordinary temperature, and this being the case it became of interest to try whether any change took place when parachlorortho-

bromorthonitrophenol, m. p. 125° , was heated with a small quantity of bromine; for this purpose—

I. 5 grams of parachlororthobromorthonitrophenol was dissolved in the minimum quantity of glacial acetic acid and heated at 100° in a bottle with one-tenth of a molecular proportion of bromine. From the crystalline form of the potassium salt, and also from the appearance and melting point of the phenol itself, it was concluded that the compound was not altered by this treatment.

II. 5 grams of parachlororthobromorthonitrophenol was dissolved in glacial acetic acid and heated for several hours at 100° with one-fifth molecular proportion of bromine.

The product on conversion into the potassium salt was obtained in red laminae identical in appearance with that obtained by brominating parachlororthonitrophenol at the higher temperature, and the compound obtained on treating the salt with acid and crystallising from alcohol melted at 119° .

III. 5 grams of parachlororthobromorthonitrophenol was dissolved in glacial acetic acid and heated as in the last experiment with half a molecular proportion of bromine. A considerable amount of decomposition had taken place in this instance, and some of the product was insoluble in potassium carbonate solution. The potassium salt was, however, obtained in plates, and the phenol from this melted at 119° .

This compound was, in all probability, orthochloroparabromorthonitrophenol, and in order to verify this a portion was heated with bromine and water, and the resulting quinone-derivative analysed as follows:—

5 grams of the substance was heated with four molecular proportions of bromine and water in the usual manner. The product obtained was crystallised from acetic acid. It contained both chlorine and bromine. A specimen dried at 100° was analysed.

0.2349 gram gave 0.4350 gram $\text{AgCl}(\text{AgBr})_3$.

	Theory. $\text{C}_6\text{ClBr}_3\text{O}_2$.	Found.
Cl.....	} 72.59 per cent.	72.21 per cent.
Br.....		

The production of chlorotribromoquinone from this compound, and of bromanil from parachlororthobromorthonitrophenol, leaves no doubt that it was orthochloroparabromorthonitrophenol.

Potassium Orthochloroparabromorthonitrophenol.—This salt has been already described in a previous portion of the paper. It may be added, however, that in addition to its differing in crystalline form from potassium parachlororthobromorthonitrophenol it is much lighter in colour than the latter.

Barium Orthochloroparabromorthonitrophenol.—This is obtained as an orange-yellow precipitate when barium chloride is added to a solution of the potassium salt in water; it is very similar in appearance to the corresponding derivative of the isomeric compound.

Calcium Orthochloroparabromorthonitrophenol.—This salt forms red crystals, much darker in colour than the isomer and differing in the amount of water of crystallisation it contains. It loses 3 mols. H_2O at $100\text{--}120^\circ$, but does not lose the whole until heated for a considerable time at 250° .

- I. 0.3245 gram lost 0.0601 gram at $100\text{--}250^\circ$ and gave 0.0681 gram CaSO_4 .
 II. 0.2301 gram gave 0.0471 CaSO_4 .

	Theory. $(\text{C}_6\text{H}_2\text{ClBrNO}_3)_2\text{Ca}, 7\text{OH}_2$.	Found.	
		I.	II.
H_2O	18.83 per cent.	18.52	— per cent.
Ca.....	5.97 „	6.16	5.99 „

Orthochloroparabromorthonitrophenol was prepared, for the sake of comparison with that obtained by isomeric transformation, from parabromorthonitrophenol, m. p. 88° , by chlorinating it in acetic acid solution.

The potassium and calcium salts agree in all respects with those previously described. The following results have been obtained on analysis:—

Potassium Salt.

0.2072 gram dried at 100° gave 0.0605 gram K_2SO_4 .

	Theory. $\text{C}_6\text{H}_2\text{ClBrNO}_3\text{K}$.	Found.
K.....	13.43 per cent.	13.08 per cent.

Calcium Salt.

0.2346 gram lost 0.0438 gram at $100\text{--}250^\circ$, and gave 0.0479 CaSO_4 .

	Theory. $(\text{C}_6\text{H}_2\text{ClBrNO}_3)_2\text{Ca}, 7\text{H}_2\text{O}$.	Found.
H_2O	18.83 per cent.	18.62 per cent.
Ca	5.97 „	5.96 „

The melting point of pure orthochloroparabromorthonitrophenol is 117° . It has been found, however, that if it be mixed with the slightest trace of the isomeride, the melting point is considerably raised. This will perhaps account for the slightly higher melting point of the compound when it is obtained from its isomeride.

Although the foregoing results are, as regards theoretical considerations, somewhat involved, there are a few points in connection with them which demand attention.

It is seen that by the action of bromine and water at 100° on dichlorororthonitrophenol, that portion of the substance which is not converted into a quinone-derivative remains unaltered, and it thus differs from dibromorthonitrophenol, which, when similarly treated, yields, as I have already shown (this vol., p. 147), among other compounds orthobromoparaorthodinitrophenol (m. p. 116°), the second nitro-group being introduced by means of the nitric acid produced from the nitroxyl liberated in the formation of bromanil. It might, therefore, have been expected that a chlorodinitrophenol would have been obtained from dichlorororthonitrophenol. According to Petersen (*Annalen*, **157**, 164, and *Ber.*, **6**, 370), when dichlorororthonitrophenol is warmed with concentrated nitric acid, it yields parachlorodiorthonitrophenol (m. p. 80.5°), and it may therefore be inferred from this that the nitric acid generated in the reaction between dichlorororthonitrophenol and bromine is not sufficiently concentrated to displace the more firmly attached chlorine-atom.

It will, however, at first sight appear anomalous that nitric acid should displace the chlorine-atom occupying the ortho-position in dichlorororthonitrophenol, and the bromine-atom occupying the para-position in dibromorthonitrophenol.

Dichlorororthonitrophenol.

Parachlorodiorthonitrophenol.

Dibromorthonitrophenol.

Orthobromoparaorthodinitrophenol.

Dr. Armstrong has shown, however (*Jour. Chem. Soc.*, 1875, 520) that *parabromodiorthonitrophenol* is easily transformed by bromine into the isomeric *orthobromoparaorthodinitrophenol*, and therefore the reaction between nitric acid and dibromorthonitrophenol is probably in the first stage precisely similar to that between nitric acid and dichlorororthonitrophenol; that is to say, the bromine-atom in the ortho-position is displaced by NO_2 . The *parabromodiorthonitrophenol* is, however, no sooner formed than it undergoes isomeric change from the presence of free bromine, which, at the temperature

employed, would be liberated by even a small quantity of nitric acid in excess.

The formation of the quinone-derivatives from these halogen-nitrophenol compounds appears to be in the strictest accordance with what might have been expected, thus:—dichlororthonitrophenol and bromine yield chlorotribromoquinone; dichloroparanitrophenol and bromine yield dichlorodibromoquinone; in like manner parachlorororthobromonitrophenol yields tetrabromoquinone, and lastly orthochloroparabromonitrophenol chlorotribromoquinone.

Dichlororthonitrophenol.

Chlorotribromoquinone.

Dichloroparanitrophenol.

Metadichlorometadibromoquinone.

Parachlorororthobromonitrophenol.

Tetrabromoquinone.

Orthochloroparabromonitrophenol.

Chlorotribromoquinone.

It will, I think, be admitted that the above concurrence with theoretical views sufficiently justifies my adopting these decompositions as a means of establishing the constitution of the two isomeric chlorobromonitrophenols.

With reference to the isomeric change of parachlorororthobromonitrophenol to orthochloroparabromonitrophenol, whatever may be the nature of the reaction, it appears to take place more easily when parachlororthonitrophenol is treated with bromine at 100° (and possibly also in Dr. Armstrong's experiment, to which I have already

referred, when parachlorodiorthonitrophenol is similarly treated), than when parachlororthobromonitrophenol is heated with a small quantity of bromine.

Parachlororthobromonitrophenol. M. p. 125°.

Orthochloroparabromonitrophenol. M. p. 117°.

This may be because it occurs simultaneously with the exchange of hydrogen for bromine. It is well known that ortho- and para-nitrophenols are incapable of exchanging more than two atoms of hydrogen for halogen,* and it would therefore be expected that a dihalogen-derivative such as parachlororthobromonitrophenol would be more or less indifferent towards reagents. Since no other compound is formed, there can be no doubt whatever that the change is intramolecular.

I hope to still further continue my experiments in this direction.

In conclusion, I must again express my thanks to Professor Armstrong for his much-valued advice.