CCC.—*The Labile Nature of the Halogen Atom in Organic Compounds. Part VI. The Action of Titanous Chloride and of Ammonia on Representative Halogen Compounds.*

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It has already been shown that certain types of organic halogen compounds possess marked oxidising properties, and previous papers in this series have dealt with the removal of the halogen atom from such compounds on treatment with various reducing agents. The reduction of the halogen-substituted nitroparaffins by hydrazine hydrate was examined by Macbeth and Pratt (T., 1921, **119**, 1356), and the work was extended to the action of acid reducing agents,

such as titanous chloride, on a similar series of compounds (Henderson and Macbeth, this vol., p. 892). It was shown that under certain conditions of molecular structure the halogen atom was removed, and the nitro-group attacked, during titanium reductions; and attention was directed to the fact that such labile halogen atoms might be regarded as possessing an electropositive character. The action of hydrazine on a further series of substances containing this characteristic type of electropositive halogen was studied by Hirst and Macbeth (this vol., pp. 904, 2169), and it was found that solutions of hydrazine hydrate were readily oxidised by these compounds, nitrogen being quantitatively liberated. The substances found to be reactive include the bromo-derivatives of certain diketones, the chloro- and bromo-derivatives of the malonic esters, and nitrogen-haloids such as the chloroamides, succinchloroimide, and the sulphonchloroamides. It seemed of interest further to extend the work and determine if the halogen atoms in compounds of the above type are susceptible to reduction by titanous salts, and if the oxidising power of the substances is sufficient to liberate nitrogen from ammonia, parallel to the reaction observed with hydrazine hydrate.

The nitrogen-haloids are found to be readily reduced by solutions of titanous chloride, the reaction taking place quantitatively in the cases examined. A quantity of the reagent equivalent to two atoms of hydrogen is required for the reduction of the gram-molecular quantity of the sulphonchloroamides, four equivalents being required for the sulphonchloroamides. The reactions are expressed in the following general equations :

N-Chloroacetanilide, acetobromoamide, succinchloroimide, and succinbromoimide are also quantitatively reduced, a quantity of titanous chloride solution equivalent to two atoms of hydrogen being required for the reduction of the gram-molecular quantity of each of these compounds.

Mono- and di-bromomalonamide are also acted upon by titanous chloride, the bromine atoms being removed in the reduction. Two, and four, equivalents of hydrogen are required for the reduction in the respective cases.

Nitromalonic ester requires six hydrogen equivalents for the reduction of the nitro-group, and ethyl bromonitromalonate requires eight equivalents for the reduction of the gram-molecular quantity.

The bromine atom is therefore removed from the bromonitro-ester during the reaction. This behaviour is in contrast with that of monobromonitromethane on the one hand and that of the bromomalonic esters on the other. The halogen atom in the nitroparaffin withstands the action both of titanous salts and of hydrazine, and the bromomalonic esters, although reactive with hydrazine, are only partly reduced after prolonged treatment with titanous chloride. As the titanium reductions were carried out under similar conditions in all cases, the resistance to reduction can only be ascribed to a difference in the reactivity of the compounds. Marked differences in the reactivities are to be expected from the point of view of the alternate effect in the molecule. The polarities of the oxygen atoms of the nitro-group in bromonitromethane do not endow the halogen atom with an electropositiveness sufficient to make it reactive with either hydrazine or titanous salts; in bromonitromalonic ester, the effect of the nitro-group is reinforced by that of the carbethoxy-groups and the very positive bromine atom is readily removed both by hydrazine and by titanous chloride; and in the bromomalonic esters the effect of the carbethoxy-groups makes the halogen sufficiently positive to react with hydrazine, but in the absence of the reinforcing effect of the nitro-group the halogen is not of a sufficiently electropositive nature to be susceptible to reduction by titanous salts.

Some observations have already been made on the action of organic halogen compounds on ammonia. Hoffmann (*Ber.*, 1882, **15**, 407) pointed out that aliphatic bromo-amides oxidise ammonia, liberating nitrogen. Willstätter and Hottenroth (*Ber.*, 1904, **37**, 1780) later showed that the bromine atom is removed from ethyl bromonitromalonate when gaseous ammonia is passed into an ethereal solution of the ester, the product being the ammonium salt of ethyl nitromalonate; the same product is obtained when the ester is shaken with strong aqueous ammonia. In contrast with this, it was noted that concentrated aqueous solutions of ammonia acted on methyl bromonitroacetate on long standing, but the halogen atom was not removed, as the product of the reaction was found to be bromonitroacetamide. This behaviour is to be expected, for the halogen in bromonitroacetic ester is not of so positive a character as the bromine in the corresponding malonate, the latter being subjected to the influence of an additional carbethoxy-group.

More recently, Short (*T.*, 1921, **119**, 1445) has shown that the halogen atom is removed from *N*-chloroacetanilide by the action of ammonia, and has based a method of estimation on measurement of the nitrogen evolved when a stream of dry gaseous ammonia is passed into a solution of the halogen compound in dry benzene. In

the present work it is found that ammonia is readily oxidised by many nitrogen haloids, and measurement of the nitrogen evolved shows that the reaction probably takes place quantitatively. The results obtained, however, are slightly low and the reaction cannot be recommended as the basis of a method of estimation, not only on account of the low results obtained, but also by reason of its cumbersome nature compared with the hydrazine method.

Succinchloroimide and succinbromoimide react vigorously with concentrated aqueous solutions of ammonia, the results obtained being from 1—4 per cent. low when calculated according to the equation

Sulphondichloroamides also react readily with ammonia, but the results obtained in such cases are also about 3 per cent. low.

Aqueous ammonia was found to be without reducing action at the ordinary temperature on the bromomalonic esters, bromomalonamides, the halogen derivatives of diketones such as acetylacetone, 1:1-dimethylcyclohexane-3:5-dione, and cyclohexanespirocyclohexane-3:5-dione. Potassium derivatives of sulphonmonochloroamides, such as chloramine T, were also found to be unattacked.

EXPERIMENTAL.

The titanium solutions employed in the reductions were prepared by boiling 500 c.c. of commercial titanous chloride (15 per cent. solution) with 800 c.c. of concentrated hydrochloric acid for a few minutes. The resulting solution was diluted with 3.5 litres of water and transferred to a storage apparatus of the usual type. The solution was standardised with methylene-blue and potassium chlorate.

In the estimations, the substance under examination was boiled gently under reflux for about thirty minutes with an excess of the titanous chloride solution, a slow stream of carbon dioxide being passed through the apparatus during the entire reduction. After cooling, the excess of titanous chloride was determined by direct titration with a standardised solution of iron alum. 19,000 C.c. of the titanous chloride solution were found to be equivalent to 2 grams of hydrogen, so 1 c.c. of the solution corresponds with 0.001866 gram of chlorine or 0.004206 gram of bromine, if the reduction follows the course

The apparatus employed in the estimations with ammonia consists essentially of a narrow-mouthed, graduated cylinder (50 c.c.), a burette, and a 100 c.c. Tennant nitrometer with second limb attach-

ment. The substance under examination is placed in the graduated vessel and covered with a little water. A two-holed stopper is fitted into the mouth of the vessel, the burette being attached through one of the holes whilst a side tube leading to the nitrometer is fitted into the other. The nitrometer is filled with dilute hydrochloric acid. An excess of concentrated aqueous solution of ammonia (d 0.880) is slowly run in from the burette, and the nitrogen evolved drives air over into the nitrometer. The burette is now filled with concentrated hydrochloric acid coloured with litmus, and this is run into the graduated flask until excess of acid is present. The whole apparatus is left for about thirty minutes, and the gas in the nitrometer then measured at atmospheric pressure. The volume of liquid introduced into the graduated vessel is noted and deducted from the volume of the gas measured in the nitrometer.

N-Chloroacetanilide.—0.3743 Gram was washed into a small flask and boiled under reflux with 50 c.c. of titanous chloride solution, 39.7 c.c. being required for the reduction. The result corresponds with 19.79 per cent. of chlorine, the percentage purity of the sample being 94.67. Estimation with hydrazine hydrate gave a value of 19.65 per cent. of chlorine, which corresponds with 94.0 per cent. of *N*-chloroacetanilide in the sample.

Potassium Benzenesulphonchloroamide.—A sample was dried on the water-bath, and 0.2398 gram, when heated under reflux with titanous chloride solution, required 19.4 c.c. for reduction. The result corresponds with 15.1 per cent. of chlorine (Theoretical, 15.46 per cent.).

Benzenesulphondibromoamide.—On heating 0.1500 gram of an impure sample of this substance under reflux with titanous chloride solution, 10.1 c.c. of the reagent were required for the reduction. The result corresponds with 28.31 per cent. of bromine, present as NBr , and the percentage purity of the sample is 56.18. Estimations with hydrazine and with potassium iodide gave an average value of 56.5 per cent. for the purity of the compound.

Acetobromoamide.—0.2628 Gram required 16.8 c.c. of titanous chloride for reduction. The bromine present as NBr therefore amounts to 26.88 per cent., and the sample contains 46.43 per cent. of acetobromoamide. Estimations by the hydrazine method gave a value of 26.84 for the bromine content, corresponding with a percentage purity of 46.3.

Potassium 2-Nitrotoluene-4-sulphonchloroamide.—An aqueous solution of this compound was prepared containing 1.4566 grams in 25 c.c., and 2.5 c.c. of this solution, on being heated under reflux with titanous chloride, required 35.89 c.c. for complete reduction. The molecular quantity therefore requires a volume of titanous

chloride solution equivalent to 7.53 (approximately 8) grams of hydrogen. The halogen atom is therefore removed in the reduction.

Dichloramine T.—A commercial sample was examined and 0.2396 gram required 34.57 c.c. of titanous chloride for reduction. The sample therefore contains 90.7 per cent. of *p*-toluenesulphondichloroamide. The substance reacts readily with ammonia, nitrogen being liberated almost quantitatively. 0.3580 Gram was found to liberate 21.4 c.c. of nitrogen at 16.5° and 740 mm. This corresponds with a content of 87.7 per cent. of the dichloroamide, the result being about 3 per cent. lower than the values obtained by other methods.

Succinchloroimide was quantitatively reduced by titanous chloride, 0.1336 gram requiring 19.05 c.c. of the reagent for complete reduction. This corresponds to a percentage purity of 100.1. The compound reacts with ammonia with the rapid evolution of nitrogen. 0.4020 Gram liberated 24.2 c.c. of nitrogen at 14° and 733 mm., which gives a value for the percentage purity of 98.74. Estimations by the potassium iodide, thiosulphate, and hydrazine methods showed the sample to be pure, and the results obtained with ammonia are therefore low.

Succinbromoimide.—A pure sample was examined and gave concordant results in hydrazine, thiosulphate, and titanium estimations. The ammonia value was again low. 0.6920 Gram reacted quickly with ammonia and liberated 30.4 c.c. of nitrogen at 16.5° and 736 mm., which gives a value of 95.63 per cent. for the purity of the sample.

Ethyl Nitromalonate.—An alcoholic solution was prepared containing 2.05 grams of nitromalonic ester in 25 c.c., and 2 c.c. of this solution were heated under reflux with titanous chloride solution; 45.1 c.c. of the reagent were required for the reduction. The molecular quantity, therefore, requires a volume of the reagent equivalent to approximately 6 grams of hydrogen, so the reduction of the nitro-group is quantitative.

Ethyl Bromonitromalonate.—An alcoholic solution was prepared containing 2.84 grams in 25 c.c., and 2 c.c. required 59.6 c.c. of titanous chloride for complete reduction. The molecular quantity therefore requires a volume of the reagent equivalent to 7.84 grams (approximately 8 grams) of hydrogen. The bromine atom is therefore removed in the reduction.

Ethyl monobromo-, dibromo-, and isobutylbromo-malonates were not reduced by titanous chloride solution under ordinary conditions, but on prolonged boiling under reflux of alcoholic solutions of the esters with excess of the reagent reduction took place, upwards of 20 per cent. of the ester being acted upon.

Ethyl acetylbromomalonate was unattacked by titanous chloride even after heating under reflux for two hours.

Monobromomalonamide.—0.1884 Gram was dissolved in 20 c.c. of alcohol and gently boiled with 30 c.c. of titanous chloride under reflux for half an hour. 19.0 C.c. of the reagent were oxidised in the reaction, so the molecular quantity of bromomalonamide requires a volume of reagent equivalent to 1.92 grams (approximately 2 grams) of hydrogen for reduction, and therefore the bromine atom is quantitatively removed. The compound is without oxidising action on ammonia.

Dibromomalonamide.—0.2683 Gram was dissolved in 20 c.c. of alcohol and heated under reflux with 50 c.c. of titanous chloride solution. 38.36 C.c. of the reagent were oxidised in the reaction, so the molecular quantity of dibromomalonamide requires a volume of the reagent equivalent to 3.92 grams (approximately 4 grams) of hydrogen for reduction. The bromine atoms are therefore removed in the reaction.

Monobromomalonmethylamide was not fully reduced by titanous chloride after treatment extending over half an hour. 0.2088 Gram oxidised 16.8 c.c. of the reagent, which corresponds with an 88.5 per cent. reduction.

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[Received, August 22nd, 1922.]