CXXVI.—*Diazohydroxylamino-compounds and the Influence of Substituting Groups on the Stability of their Molecules. Part II.*

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IN a previous communication (this vol., p. 767), a number of diazohydroxylamino-compounds were described, all of which might be considered as mono-substitution products of the parent substance, benzenediazohydroxylamino-*p*-toluene,

and containing their various substituting groups in the ring A in various positions relative to the azo-grouping already present. The object of the present paper is to describe experiments carried out with a view to determine the influence of these various substituting groups on the general stability of the molecule. The problem was attacked in two ways: first, the action of bromine dissolved in an organic solvent was tried, and secondly, the effect of treating each separate compound with an acid under definite conditions of temperature and concentration, that is, under known conditions, was determined.

The Action of Bromine in Chloroform Solution.

The initial experiments on the action of bromine in chloroform solution on these substances seemed, at the outset, to lead to the general conclusion that the method would form an excellent means of obtaining a qualitative idea of the stability of the various compounds on which it was tried, and hence information as to the effect produced by the various substituting groups on the stability of the molecule containing them. A closer examination, however, of the reaction revealed the fact that, not only did bromine act as a decomposing agent towards the compound in question, but that it also acted as a substituting agent, and that both these processes took place at one and the same time in the case of some of the compounds concerned, whilst in the case of others, the one or the other took place as the case might be; as a consequence of this, the action of bromine could hardly be considered as one throwing any great light on the object in view. In consideration, however, of the fact that some few new diazohydroxylamino-compounds were isolated by this means, and that in general the results of the action are in keeping, at least in degree with those obtained by the second or better method, it was determined to quote this work in some detail, and the results derived from it will be found in the experimental part.

The Action of Hydrochloric Acid on the Diazohydroxylamino-compounds.

As was previously shown (*loc. cit.*), all diazohydroxylamino-compounds are affected by hydrochloric acid, which apparently is much more powerful when acting in solution in an organic solvent. The decomposing action of this acid is a very simple one, as may readily be proved by qualitative means: a diazonium compound and a hydroxylamine (or a product of its rearrangement) results thus:

This decomposing action was now made use of as a means of ascertaining quantitatively how much of each separate diazohydroxylamino-compound was decomposed when treated with the acid under as comparable conditions as possible. The method used consisted in allowing the acid, in definite quantity at a suitable concentration and at a definite temperature, to act on the variously substituted diazohydroxylamino-compounds for definite lengths of time, in order to determine exactly in each case what effect ortho-substitution has over and above para- and meta-substitution, and, furthermore, to derive, where possible, any information respecting the relative effects of each specific substituting group on the stability of the molecule. Dealing, as is obvious, with a whole series of compounds all possessing different solubilities in various solvents, it was hardly possible to lay down any definite conditions to be observed throughout. The factor, temperature, at which the decompositions were carried out was, however, fixed at 15°, and owing to the different solubilities shown by the various substances, all experiments could not be carried out in the same solvent. A further difference in the examination of the various substances which it was necessary to observe was occasioned by the wide differences existing between the ease with which some were decomposed and others not, necessitating the use of varying amounts of hydrochloric acid compatible with experimental exactness.

A known amount of the substance to be examined, namely, 0.25 gram, was dissolved in a definite quantity in the organic solvent (either chloroform or glacial acetic acid), and to it was added a definite volume of the same solvent saturated with dry hydrogen

chloride at 15°. The mixture was kept at 15° for a definite time, when it was treated in such a manner as to isolate in aqueous solution the diazonium compound formed, the actual amount of the same being estimated by treatment at the boiling point with 2*N*-sulphuric acid, the nitrogen evolved being collected. From the volume, temperature, and pressure of the gas obtained, it was an easy matter to determine the actual amount of the diazohydroxylamino-compound decomposed under the conditions employed.

A series of experiments was carried out on the variously substituted diazohydroxylamino-compounds on the above lines, the results of which are tabulated below.

Substance.	Solution.	Composition of decomposing solution.	Duration of experiment in hours.	Dry nitrogen at N.T.P. obtained in c.c.	Per- centage decom- position.
Benzenediazohydroxyl- amino- <i>p</i> -toluene.	CHCl ₃	15 c.c. CHCl ₃ 15 c.c. CHCl ₃ (saturated with HCl)	22	17.9	72.6
<i>o</i> -Bromobenzenediazo- hydroxylamino- <i>p</i> - toluene.	CHCl ₃	15 c.c. CHCl ₃ 15 c.c. CHCl ₃ (saturated with HCl)	22	6.48	35.4
<i>p</i> -Bromobenzenediazo- hydroxylamino- <i>p</i> - toluene.	CHCl ₃	15 c.c. CHCl ₃ 15 c.c. CHCl ₃ (saturated with HCl)	22	11.5	62.8
<i>m</i> -Bromobenzenediazo hydroxylamino- <i>p</i> - toluene.	CHCl ₃	15 c.c. CHCl ₃ 15 c.c. CHCl ₃ (saturated with HCl)	22	16.36	89.4
<i>o</i> -Tolyldiazohydroxyl- amino- <i>p</i> -toluene.	C ₂ H ₄ O ₂	30 c.c. C ₂ H ₄ O ₂ 10 c.c. C ₂ H ₄ O ₂ (saturated with HCl)	2	7.68	32.4
<i>p</i> -Tolyldiazohydroxyl- amino- <i>p</i> -toluene.	C ₂ H ₄ O ₂	30 c.c. C ₂ H ₄ O ₂ 10 c.c. C ₂ H ₄ O ₂ (saturated with HCl)	2	11.79	49.8
<i>m</i> -Tolyldiazohydroxyl- amino- <i>p</i> -toluene.	C ₂ H ₄ O ₂	30 c.c. C ₂ H ₄ O ₂ 10 c.c. C ₂ H ₄ O ₂ (saturated with HCl)	2	6.38	26.9
<i>o</i> -Nitrobenzenediazo- hydroxylamino- <i>p</i> -toluene.	C ₂ H ₄ O ₂	20 c.c. C ₂ H ₄ O ₂ (saturated with HCl)	12	3.55	16.3
<i>p</i> -Nitrobenzenediazo- hydroxylamino- <i>p</i> -toluene.	C ₂ H ₄ O ₂	20 c.c. C ₂ H ₄ O ₂ (saturated with HCl)	12	13.44	61.92
<i>m</i> -Nitrobenzenediazo- hydroxylamino- <i>p</i> -toluene.	C ₂ H ₄ O ₂	20 c.c. C ₂ H ₄ O ₂ (saturated with HCl)	12	10.98	50.6
<i>o</i> -Carbethoxybenzenedi- azohydroxylamino- <i>p</i> -toluene.	C ₂ H ₄ O ₂	20 c.c. C ₂ H ₄ O ₂ (saturated with HCl)	12	2.54	13.5
<i>p</i> -Carbethoxybenzenedi- azohydroxylamino- <i>p</i> -toluene.	C ₂ H ₄ O ₂	20 c.c. C ₂ H ₄ O ₂ (saturated with HCl)	12	6.79	36.3
<i>m</i> -Carbethoxybenzenedi- azohydroxylamino- <i>p</i> -toluene.	C ₂ H ₄ O ₂	20 c.c. C ₂ H ₄ O ₂ (saturated with HCl)	12	9.07	48.4

NOTE.—0.25 gram was used in each case. Temperature 15°.

Discussion of Results.

The main fact to be deduced from the foregoing series of experiments is that when a diazohydroxylamino-compound is substituted by some group or other in the ortho-position relative to the one occupied by the azo-group, then the general stability of the molecule is sensibly increased. In other words, the effect of an ortho-substituent on the action of decomposing agencies is a protective one; it may, in fact, be compared with that similar phenomenon shown by the esters of differently substituted aromatic acids towards hydrolysis, when, as is well known, the presence of a substituent grouping in the ortho-position with respect to the carboxyl group greatly retards the same (compare V. Meyer and A. M. Kellas, *Zeitsch. physikal. Chem.*, 1897, **24**, 243; *Ber.*, 1895, **28**, 1258). Similar phenomena are also observed in the behaviour of aromatic amines when similarly substituted relative to the amino-group (compare A. Werner, *Lehrbuch der Stereochemie*). The protective influence, as it has been termed, which substituents in the ortho-position relative to the azo-group exert on the stability of the molecules of these diazohydroxylamino-compounds towards decomposing influences, from analogy may therefore be said to be further examples of the well-known phenomenon of steric hindrance.

A much better idea of the differences existing in the decomposability of isomeric compounds containing their substituting group in the ortho-, para-, and meta-positions respectively can be gained by a glance at the foregoing table. With the exception of the methyl substituted derivatives, it will readily be observed that the ortho-compounds all show the least amount of decomposition compared with that of their para- and meta-isomerides respectively, the decomposing influences, it will be noted, being identical in the case of each set of isomerides.

The hindering influence against decomposition exerted by groups situated in the ortho-position with respect to the azo-group in these compounds is therefore amply demonstrated, and is quite comparable with other well-known cases of steric hindrance. A comparison of the influence of the various substituting groups themselves on the stability of the substances regarding the question as to which exercises the greatest hindering effect cannot be entered into by reason of the fact that although the decomposing influences made use of are comparable for any three isomeric substances, yet these influences, naturally changed for reasons before stated, are in no way comparable where substances containing different substituting groups are concerned.

The results obtained from the action of bromine on these diazohydroxylamino-compounds, which are of interest as throwing a light on the problems, will be found detailed with each specific reaction noted.

EXPERIMENTAL.

Action of Bromine in Chloroform Solution on Benzenediazohydroxylamino-p-toluene.

A solution of 0.45 gram of benzenediazohydroxylamino-*p*-toluene in 15 c.c. of chloroform was mixed with 6.4 c.c. of a 10 per cent. solution of bromine, also in chloroform at 10°. After rapidly reducing the slight rise in temperature produced, the mixture was kept for ten minutes, and the crystals which separated were collected; these were proved qualitatively to consist of a bromo-substitution product of the original substance. The chloroform mother liquor was extracted thoroughly with water, and the aqueous extract on testing with an alkaline solution of β -naphthol was found to contain the merest trace of a diazonium compound. On evaporation of the chloroform solution, a few pale brown crystals separated, and a very faint odour of a nitroso-compound was noticeable. Under the above conditions the action of bromine appears to be almost entirely one of substitution, practically no fission of the molecule taking place.

Action of Bromine in Chloroform Solution on the Methyl Derivatives of Benzenediazohydroxylamino-p-toluene.

(a) *o*-Tolyldiazohydroxylamino-*p*-toluene.—A chloroform solution of the above compound was treated with two molecular proportions of bromine; a considerable rise in temperature took place, and, after keeping for ten minutes at 18°, the solution was extracted with water and the chloroform evaporated in a vacuum. A semi-crystalline residue was left, which, after drying on a porous plate, was recrystallised:

0.1275 gave 14.7 c.c. N_2 at 21° and 758 mm. $N = 13.09$.

0.1375 „ 0.0796 AgBr. $Br = 24.95$.

$C_{14}H_{14}ON_3Br$ requires $N = 13.13$; $Br = 25.00$ per cent.

The reactions of this substance are almost identical with those of the diazohydroxylamino-compound from which it is derived, and it is thus a *monobromo-o-tolyldiazohydroxylamino-p-toluene*.

It melts at 120.5°, and crystallises in stumpy, broad, flat needles of a fine yellow colour, which turn brown on exposure to light and air. It is very readily soluble in benzene, chloroform, and acetone, but more sparingly so in alcohol, ether, or light petroleum.¹

From the porous plate on which the crude bromination product

was dried, a small quantity of a bright green oil, showing all the properties of, and being identical with, *p*-nitrosotoluene, was isolated.

On adding the aqueous extract of the chloroform solution to an alkaline solution of β -naphthol, a considerable quantity of a deep scarlet dye (*bromo-o-tolylazo- β -naphthol*) was precipitated, which, on crystallisation from glacial acetic acid, melted at 171° :

0.1563 gave 0.0850 AgBr. Br = 23.14.

$C_{17}H_{13}ON_2Br$ requires Br = 23.46 per cent.

Bromine thus apparently exercises primarily a substituting influence, the substituted product subsequently suffering decomposition.

(b) *m-Tolyl-diazohydroxylamino-p-toluene*.—By a similar action of bromine in chloroform solution this compound yielded *monobromo-m-tolyl-diazohydroxylamino-p-toluene*, which melts at 155° and crystallises in bright yellow, long, slender, hair-like needles; these are very sparingly soluble in light petroleum or alcohol, more readily so in benzene, ether, or acetone, and very readily so in chloroform :

0.1125 gave 12.7 c.c. N_2 at 20.5° and 762 mm. N = 12.93.

0.1341 „ 0.0794 AgBr. Br = 25.19.

$C_{14}H_{14}ON_3Br$ requires N = 13.3 ; Br = 25.00 per cent.

The substance is very much more stable than the diazohydroxylamino-compound from which it is derived, otherwise the reactions of the two substances are almost identical.

A bright scarlet dye (*bromo-m-tolylazo- β -naphthol*) was obtained from the aqueous extract of the chloroform solution, and, when pure, melted at 145° :

0.1271 gave 0.0696 AgBr. Br = 23.30.

$C_{17}H_{13}ON_2Br$ requires Br = 23.46 per cent.

Hence the action of bromine in this case is practically identical with that obtained from the ortho-isomeride.

(c) *p-Tolyl-diazohydroxylamino-p-toluene*.—In this case also the action of bromine gave rise to a *monobromo*-substitution product, which crystallises in long, slender, bright yellow needles melting at 102° . With the exception of alcohol and light petroleum, the substance is very readily soluble in the common organic solvents :

0.1131 gave 0.0670 AgBr. Br = 25.20.

$C_{14}H_{14}ON_3Br$ requires Br = 25.00 per cent.

Its reactions are practically identical with those of the compound from which it is derived.

A considerable quantity of *p*-nitrosotoluene was also isolated as a result of the reaction, and the bright red dyestuff obtained by coupling the diazonium salt obtained from the aqueous extract of the original reaction mixture with β -naphthol was found to be identical

with *p*-tolylazo- β -naphthol, and thus to contain no bromine, differing in this respect from the dyes obtained in the case of the ortho- and meta-isomerides. Bromine thus has not only a substituting action, but also a decomposing one, both apparently taking place simultaneously.

Action of Bromine in Chloroform Solution on the Carbethoxybenzenediazohydroxylamino-p-toluenes.

(a) *o*-Carbethoxybenzenediazohydroxylamino-*p*-toluene.—A mono-bromo-substitution product of this was obtained in almost theoretical yield; the *bromo-o-carbethoxybenzenediazohydroxylamino-p-toluene* obtained is of a pale yellow colour, melts at 148° , and crystallises in stellate aggregates of thin, sharply-pointed needles. It is very sparingly soluble in light petroleum, alcohol, or glacial acetic acid, but very readily so in benzene or chloroform, and its reactions are similar to those of the parent substance:

0.1499 gave 0.2780 CO_2 and 0.0642 H_2O . $\text{C} = 50.56$; $\text{H} = 4.76$.

0.1285 „ 12.8 c.c. N_2 at 20° and 768 mm. $\text{N} = 11.52$.

0.1404 „ 0.0699 AgBr. $\text{Br} = 21.18$.

$\text{C}_{16}\text{H}_{16}\text{O}_3\text{N}_3\text{Br}$ requires $\text{C} = 50.80$; $\text{H} = 4.21$; $\text{N} = 11.11$; $\text{Br} = 21.16$ per cent.

The aqueous extract of the reaction mixture was found to contain the merest trace of a diazonium compound.

Some experiments were also carried out on the action of bromine on the same compound in glacial acetic acid solution, when it was found that its behaviour was absolutely identical to that in chloroform.

Bromine therefore acts on this compound solely as a substituting agent, the presence of a carbethoxy-group in the ortho-position with respect to the diazohydroxylamino-grouping apparently serving as a protection against the decomposing action of the halogen.

(b) *m*-Carbethoxybenzenediazohydroxylamino-*p*-toluene.—In this case no trace whatever of a bromine substituted compound could be isolated. The chloroform solution, after extraction with water, left a large quantity of a dark-coloured oil, almost entirely volatile and consisting of impure *p*-nitrosotoluene.

From the aqueous extract, by the action of alkaline β -naphthol, a dark red azo-dye (*m-carbethoxybenzeneazo- β -naphthol*), melting at 105° , was obtained:

0.1452 gave 11.00 c.c. N_2 at 19° and 745 mm. $\text{N} = 8.56$.

$\text{C}_{19}\text{H}_{16}\text{O}_3\text{N}_2$ requires $\text{N} = 8.75$ per cent.

The action of bromine in glacial acetic acid was identical with that given above, so that in both solvents its action was solely one of decomposition.

(c) *p*-Carbethoxybenzenediazohydroxylamino-*p*-toluene.—The chloroform solution on evaporation yielded an oily, semi-liquid residue, which consisted chiefly of *p*-nitrosotoluene. On extraction with light petroleum, however, an insoluble residue was obtained, too small in amount to be submitted to analysis, but which was proved to contain bromine. The aqueous extract of the chloroform, on coupling with β -naphthol, yielded a dye, which was free from bromine. Hence bromine seems to exert almost solely a decomposing influence, substitution taking place only to a very slight extent.

Action of Bromine in Chloroform Solution on the Three Mononitrobenzenediazohydroxylamino-p-toluenes.

In the case of the ortho-isomeride at the ordinary temperature, no action whatever took place, whilst at higher temperatures both decomposition and substitution were effected.

The meta-isomeride suffered only decomposition, little, if any, substitution taking place, whilst identical behaviour was observed in the case of the para-isomeride.

At low temperatures, namely, at 10—15°, the ortho-isomeride remains absolutely unattacked after keeping for weeks, whilst the other two are only very slowly decomposed, thus demonstrating the protective action of the nitro-group in general and its greater protective action when in the ortho-position.

Action of Bromine in Chloroform Solution on the Three Monobromobenzenediazohydroxylamino-p-toluenes.

In the case of the ortho-isomeride, the action was both of a decomposing and of a substituting nature. The chief action in the case of the meta-isomeride was one of decomposition, and in the case of the para-compound almost exclusively one of substitution, the reaction therefore in general furnishing little or no criterion of the effect of the bromine atom in its three possible positions.

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