

Chemistry. — *The Action of Per-Acetic Acid and Per-Benzic Acid on the Unsaturated Aliphatic and on Aromatic Iodine Compounds.*
By J. BÖESEKEN and CH. SCHNEIDER.

(Communicated at the meeting of November 26, 1932).

It is known that in 1886 WILLGERODT discovered that the iodine bound to the aromatic C.-atom is easily chlorated to iodide dichloride, and that by the action of soda, these iodide chlorides are converted to iodoso compounds, which by oxido-reduction give rise to the formation of iodo-compounds and original iodine compound.

In 1892 (B. 25. 2632) V. MEIJER and WACHTER obtained the iodoso benzoic acid by direct oxidation of o. iodine benzoic acid¹⁾ with fuming nitric acid.

WILLGERODT obtained iodoso compounds with NaOBr B. 29, 1571 (1896) and BAMBERGER B. 33. 533 (1900) by direct oxidation with CARO's acid.

This last mode of preparation led us to the conclusion that these iodoso-compounds and iodo-compounds could be easily prepared both from the aromatic and from the aliphatic iodine-compounds by oxidation with organic per-acids, for also aliphatic iodoso compounds have been prepared by THIELE Ann. 369. 119 (1905), which he did by converting unsaturated iodine compounds as $\text{CHCl}=\text{CHI}$ with Cl_2 into the iodide chlorides, and decomposing these with soda.

The result of this investigation has quite answered our expectations, compounds could even be obtained, which were accessible by no other way.²⁾

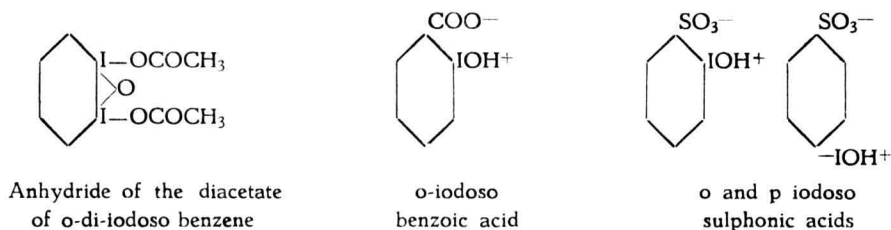
At first aromatic iodine compounds were oxidized with 8—10 % solutions of per-acetic acid in acetic acid. Then the *diacetates of the iodoso-compounds* were formed, which were oxidized no further under these circumstances. In this way were obtained the diacetates of *iodoso*

¹⁾ Iodine-benzoic acid = $\text{IC}_6\text{H}_4\text{COOH}$; iodo-benzoic acid = $\text{IO}_2\text{C}_6\text{H}_4\text{COOH}$.

²⁾ As our first communication on this subject in the meantime has been supplemented by new facts, and the insight into this reaction has undergone considerable modification, we have thought it advisable to publish it not as an addition to this communication, but independent of it as a paper by itself.

benzene, *o*-iodoso toluene, *o*-nitro-iodoso benzene, *m*-nitro-iodoso benzene, *p*. iodoso benzoic acid, and tetracetate of *m*-di iodoso benzene.

Further a diacetate of the *o*-di iodoso-benzene anhydride was formed from *o*-di iodine benzene, to which, on the strength of the analysis values and the properties the following constitution was assigned:



The *o*-iodine benzoic acid, the *o*-iodine benzene sulphonic acid and *p*-iodine sulphonic acid gave the corresponding iodoso acid, to which we give the dipole formulae; the last compound was not known, attempts to prepare it by another method, had failed.

With *per*-benzoic acid in *chloroform* the *iodo*-compounds were directly obtained, except with *o*-iodine-benzoic acid and *o*-iodine benzene sulphonic acid.

At first we thought that we had to ascribe this difference to the nature of the oxidizer; when it, however, appeared that *o*-di iodine benzene formed, besides the di-iodoso acetate anhydride mentioned before, also a little di iodo compound, and ARBUSON and MICHAILOW (J. pr. Ch. 127. 92) had found that the different behaviour of *per*-acetic and *per*-benzoic acid towards the double bond had to be attributed to the different solvent, we have oxidized iodine benzene for one part with a higher percentage of *per*-acetic acid in *chloroform*, for another part with *per*-benzoic acid in *glacial acetic acid*, and obtained a mixture of iodoso- and iodo benzene in both cases (J. pr. Ch. 131, p. 285, 1931). The stopping of the oxidation with diluted *per*-acetic acid in *glacial acetic acid* as the iodoso compound is formed must therefore be attributed to the acid solvent, which binds the iodoso base; as a salt the further oxidation is evidently hampered.

As the iodoso acids can also be considered as internal salts (the reason why we assign the dipole formula to them), the stopping of the oxidation is comprehensible.

By making use of high-percentage *per*-acetic acid, through which the acetic acid concentration is diminished, the oxidation can proceed in most cases, on the other hand by adding acetic acid to the *chloroformic* solution, the further formation of *iodo*-compounds can be impeded.

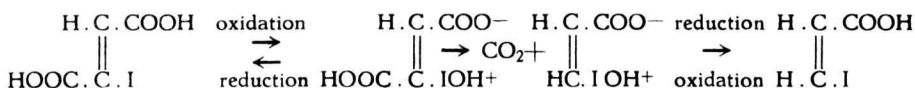
The use of high-percentage *per*-acetic acid had, besides, the advantage that some compounds, as *m*-iodoso benzene sulphonic acid, could be obtained, the preparation of which had not yet succeeded by any other way.

Oxidation of aliphatic iodine compounds.

THIELE's observation (loc. cit.) that only those compounds which had the iodine atom situated at an ethylene bond, could be converted into iodoso and iodo compounds, we could confirm by means of this direct oxidation.

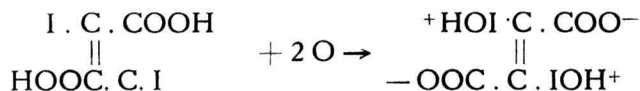
Iodoform gave a strong separation of iodine, which element was further oxidized to I_2O_5 . C_2I_2 gave C_2I_4 , neither of them an iodine oxygen compound. $C_2H_2I_2$ gave, on the other hand, with per-benzoic acid and with per-acetic acid, a white highly explosive compound with 17.7% active oxygen; probably this is *di-iodoethylene* (calculated 18.6% active oxygen).

Oxidation of iodine fumaric acid; THIELE did not succeed in preparing the iodide chloride from this; with 70% per-acetic acid we obtained *iodoso fumaric acid*, which with SO_2 rendered back the original iodine fumaric acid. Boiled in water CO_2 splits off, and it passes into *iodoso acrylic acid*. Since by careful reduction with SO_2 this compound can be converted into *iodine acrylic acid* of melting point 65° (See STOLZ B. 19, 542 (1886)), the succession of the reactions may be represented thus:



Really on oxidation with per-acetic acid this iodine acrylic acid yielded an iodoso-acrylic acid, which proves at the same time that the low-melting acid obtained by STOLZ with conc. HI from propiolic acid is the β -*cis*-iodine acrylic acid; a WALDEN reversal is not to be expected in this oxidation.

The di-iodine fumaric acid took up two active oxygen atoms; hence an iodine-iodo- or a di-iodoso fumaric acid may have been formed. Seeing that on boiling with H_2O the compound did not split off CO_2 , the latter supposition is the more probable one; for it is to be expected that on passing into the dipole state the CO_2 group becomes stable.



From an electric point of view this substance is very interesting, on account of internal compensation it will probably show no dipole effect.

The di-iodine stilbene was *not* oxidized by per-acetic acid in acetic acid solution; in chloroform solution a remarkable conversion set in.

With separation of iodine the di-chloro stilbene oxide $C_6H_5 \begin{array}{c} \diagup O \diagdown \\ C - C \\ \diagdown Cl \diagup \end{array} C_6H_5$ was obtained, an interesting example of the active part of the solvent.

In conclusion we will give a survey of the melting-points and points of decomposition of the compounds obtained:

Iodoso benzene diacetate	Mp. = 157°
Iodo benzene	Explosion p. = 211°
o-Iodo toluene	" = 212°
p-Iodo toluene	" = 230°
o-Iodoso nitrobenzene diacetate	Mp. = 146°
Iodo-nitrobenzene	= 214°
m-Iodoso nitrobenzene diacetate	Mp. = 150°
m-Iodo nitrobenzene	Expl. p. = 218°
o-Iodoso benzoic acid	Mp. = 168°
p-Iodo-benzoic acid	Expl. p. = 220°
o-Iodoso benzene sulfonic acid	Expl. p. = 196°
m- " " " " "	= 139°
p- " " " " "	= 158°

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Physics. — *The Gravity Expedition of Hr. Ms. O 13 in the Atlantic.*
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During the past summer, the Dutch Navy has again been willing to promote an expedition for determining gravity at sea; for one month and a half His Exc. the Minister of the Navy, Mr. DECKERS, has allotted a submarine for an investigation in the Atlantic. Sincere thanks are due to the Navy for this important contribution to science and likewise to the Netherlands Geodetic Commission, President Prof. Dr. J. A. A. MULLER, under whose auspices the expedition has taken place.

The object of the expedition was to investigate especially those parts of the Atlantic, where the frequency of earthquakes proves the tectonic activity of the Earth's crust, in order to be able to compare the gravity field with the fields found in other seismic regions, e. g. the East Indies and the West Indies. This would provide a base for attacking the problem of the nature of the tectonic phenomenon taking place in the Atlantic and whether it is of the same kind as what is going on in the geosynclinal areas in those other regions.

In 1926, a great many data were already obtained in the Atlantic by the expedition of Hr. Ms. K 13, but most of the stations of this trip are at a distance of about two hundred miles from each other. Con-