A PERIODIDE OF TRIPHENYLBROMMETHANE.[1]

BY M. GOMBERG.

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IN an attempt to prepare triphenyliodomethane the corresponding bromine compound was heated with finely powdered potassium iodide suspended in benzene. The solution soon turned dark red, showing the liberation of iodine from the potassium salt. The purer the bromine compound, the less iodine was set free, while prolonged boiling, even with the purest reagents, increased its yield. The benzene solution, filtered from the potassium salts, deposited, on cooling, a small crop of bluish green irridescent crystals, resembling, in their appearance and behavior, the well-known periodides of organic bases. The crystals contained both iodine and bromine, and it was therefore concluded that their formation was due to the action of the small quantity of free iodine upon the triphenylbrommethane.

Accordingly, a solution of iodine in benzene was added to a solution of the bromine compound, also in benzene. The periodide invariably separated in the form of crystals, the size of which depended upon the concentration of the solution. These crystals proved to be identical in every respect with those obtained when potassium iodide was employed.

The periodide was found to be of the composition

$$(C_6H_5)_3CBr.I_4,$$

with all the iodine held loosely, just as in the periodides of organic bases. The iodine could be titrated directly with standard solutions of sodium thiosulphate or sodium arsenite.

The periodide here described differs in some respects from the other compounds of this class. The formation of superiodides has been limited, with a few exceptions, to the nitrogen family of the elements,[2] the largest number of such superiodides being those of the organic nitrogen bases. Even the few exceptions are, after all, periodides of substances either themselves basic in their nature, or in combination with bases. The periodides of the diazo salts[3] are strictly such of bases. The superiodides of

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[1] Read at the Boston meeting of the American Chemical Society. August, 1898.

[2] Prescott, *1895* : This Journal, **17**, 779.

[3] Hantzsch *1895* : *Ber. d. chem. Ges.*, **28**, 27 4.

iodonium salts find their explanation in the fact that the iodonium compounds are bases in every other respect as well. The periodides of metals are such of *inorganic* bases. The sulphon periodides of Kastle and Hill[2] are analogous to the herapathites of Jörgensen, with substitution of an inorganic base for an organic. The periodide of triphenylbrommethane, however, has not, so far as I am aware, its analogue. It is not a periodide of a salt of a base, nor of a free base[3]. On the contrary, triphenylbrommethane is made up entirely of negative groups. The periodide is unlike those recently described by Remsen and Norris.[4] It can hardly be assumed that the iodine adds itself to any of the benzene rings in the triphenylmethane. It must be linked to the molecule trough the bromine atom.

I have shown some time ago[5] that the amount of additive iodine (or bromine) in a base is in no way proportional to, or indicative of, the basic power of the compound. And here we have an example of a periodide, with as many as four atoms of additive iodine, of a substance which has no basic properties whatever.

Triphenylbrommethane Tetraiodide, $(C_6H_5)_3CBr.I_4$.—When a saturated benzene solution of iodine is added to a solution of triphenylbrommethane in benzene, a dark granular precipitate, soon changing to crystals, is thrown down. The periodide in this form always contains a little free iodine, which is difficult to remove by mere washing with benzene. When dilute solutions of the reagents are employed, the precipitation does not take place at once, and the solution has to be set aside for some time, or gently concentrated. Slow crystallization gives larger crystals, but these also contain frequently from two to three per cent. of free iodine. The periodide can also be obtained by substituting carbon disulphide for benzene, but in this case the solutions must be more concentrated, as the periodide is quite soluble in carbon disulphide. The amount of iodine employed varied in the different experiments from one-half to three times the theoretical quantity, but in no case was the formation

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[1] *Ber. d. chem. Ges.*, **27**, 1594.

[2] *Am. Chem. J.*, **16**, 116.

[3] Such as $C_5N_5N.I_4$. (Prescott and Trowbridge: This Journal, **17**, 865.)

[4] *Am. Chem. J.*, **18**, 94, *1896*.

[5] This Journal, **18**, 377.

of either a higher or a lower periodide observed than the one here described. The yield is very good. When benzene is employed as a solvent, eighty to eighty-five per cent. of the theoretical quantity of the periodide is obtained.

For analysis, the periodide was recrystallized from warm benzene or carbon disulphide. The crystals were filtered off by means of a pump, washed with a little benzene, and dried, *in vacuo*, over sulphuric acid. The iodine was estimated in most cases by titrating weighed samples of the substance suspended in alcohol with a sodium thiosulphate solution. In some cases the iodine was estimated by reducing the periodide with zinc dust and water. The iodine was set free by a saturated solution of nitrous acid in concentrated sulphuric acid, extracted with carbon disulphide, the latter washed with a weak solution of sodium carbonate, and the iodine titrated as before. The bromine was estimated by igniting the periodide with lime and estimating the total halogen, *i. e.*, bromine and iodine together, with silver nitrate solutions. From the total mixture of silver halides, the quantity of silver iodide corresponding to the amount of iodine, as found by titration, is subtracted. The difference represents silver bromide.

The following are some of the analyses obtained on different samples of the perhalide :

I. 0.2203 gram substance gave 0.1340 gram iodine.
II. 0.3428 gram substance gave 0.2100 gram iodine.
III. 0.1641 gram substance gave 0.1027 gram iodine.
IV. 0.1495 gram substance gave 0.0914 gram iodine.
V. 0.2560 gram substance gave 0.1578 gram iodine.
VI. 0.4256 gram substance gave 0.2621 gram iodine.
0.2253 gram substance gave 0.3058 gram AgI.

	Calculated for $(C_6H_5)_3CBr.I_4$.	Found.					
		I.	II.	III.	IV.	V.	VI.
Iodine……	61.05	60.83	61.26	62.58	61.50	61.64	61.58
Bromine …	9.61	….	….	….	….	….	9.15

Estimation IV was done by previous reduction with zinc dust; all the others by direct titration.

The periodide is of a bluish-green iridescence. It can be obtained in long hexagonal prisms, or in small needle-like crystals. In two samples, obtained by slow crystallization, the crystals were hollow, the canal coinciding as nearly as could be judged with the longitudinal axis of the crystals. The exact conditions necessary for the production of such hollow crystals have not been ascertained. Only two similar cases of crystallization have been reported, so far as I could find.[1] The periodide is only slightly soluble in cold benzene ; more freely in hot. It is quite soluble in carbon disulphide. It is decomposed by alcohol and ether. When dry, and placed in a bottle, it remains unchanged for a long time ; but when exposed to the air it gradually loses iodine. It melts at 121°–122° C.

A sample was gently heated at 40°–45° C. for some time, until the color changed to a dark gray. The residue was recrystallized from petroleum ether, and by its melting-point (152° C.) and all other properties was identified as bromtriphenylmethane.

Attempts to determine the molecular weight by the cryoscopic method did not give satisfactory results.

I wish to thank Mr. W. H. Hess, who kindly helped me in this work.

ANN ARBOR, MICHIGAN.

NITRIC NITROGEN PRODUCED BY THE PEA.

BY J. L. BEESON.

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IT has been long known that the leguminous plants contain more nitrogen than they get from the soil, hence their almost universal use as soil improvers.

Hellriegel and Wilfarth in 1886 showed that the leguminosæ would not grow in sterilized sand for lack of nitrogen, but that if the sand be inoculated with water, in which the roots of a well developed plant of the variety experimented on had been soaked, the plant would at once begin to grow, rapidly developing root tubercles. Microscopic investigation showed the presence of bacteria in these tubercles. These micro-organisms are now cultivated and sold under the name of "Nitragin" for the purpose of inoculating sterile soils, that is, soils which do not contain the leguminous micro-organisms.

Later experiments have shown that each kind of leguminous plant has its own kind of bacteria, and that those from another leguminous plant will not answer for inoculation purposes.

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[1] Kebler, *1895* : *Am. J. Pharm.*, 67, 602 ; Trowbridge, *1897* : This Journal, 19, 328.