XLV.—*On the Formation of the Iodides of the Alcohol-radicles from Boghead Naphtha.*

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THE possibility of passing from the bibasic to the monobasic radicles, by the addition of hydrogen to an olefiant, through the medium of a hydracid, was first shown by M. Berthelot. The reaction with hydriodic acid is represented by the equation:—

This reaction has been of the greatest service to me in pursuing my researches upon the hydrocarbons produced during the distillation of Boghead coal.

My first experiments were made to ascertain whether homologues of benzole and of marsh gas would, by dilution, prevent the action of the hydracids on the comparatively small quantity of the olefiant present. With hydrochloric acid this would appear to be the case. I then resorted successfully to fuming hydriodic acid, having a density between 1·8 and 1·9; a less concentrated acid has little action.

360 GREVILLE WILLIAMS ON FORMATION OF IODIDES OF

The following process appeared to yield the iodides more readily than any other yet tried. The naphtha, of a boiling point corresponding with that of the olefant to be experimented on, was placed in a flask with a neck three or four feet long. About half the bulk of fuming hydriodic acid having been added, the mixture was cohobated for two or three hours. The neck was then cut off and replaced by a bent tube connected with a condensing apparatus. On applying a gentle heat, the hydrocarbons unacted on slowly distilled away. The more volatile portion having in this manner been removed, the distillation was carried on in a current of steam, until the distillate began to sink in water. The receiver was then changed and the product collected apart.

By proceeding in the manner described, I have obtained from Boghead naphtha the iodides of amyl, oenanthyl, capryl, and pelargonyl. It is evident, therefore, that Boghead naphtha may now be made to yield an almost infinite variety of products, some of them belonging to organic groups, which have, hitherto, almost escaped investigation.

The quantities of the iodides produced up to the present time, have been too small to allow direct analyses to be made: it became necessary, therefore, to employ some reaction by which a small quantity of iodide might be made to yield a comparatively large amount of a substance capable of being purified and analysed. For this purpose nothing appeared more suitable than the compound ammonias, because a very small amount of base could be made to yield a large quantity of platinum-salt.

With this intention the iodides were scaled up in strong tubes with a large excess of alcoholic ammonia, and heated to 100°C ., for twelve hours. On opening the tubes and supersaturating the fluid with hydrochloric acid, a small quantity of oil remained undissolved, which was carefully removed. The soluble portion was then evaporated nearly to dryness, to expel the alcohol and traces of hydrocarbons. The solution distilled with excess of hydrate of potassium, yielded ammonia and an oily base. On adding a great excess of solid hydrate of potassium to the mixture, the alkaloid separated almost entirely, and, after distillation, was dissolved in hydrochloric acid and treated with an excess of chloride of platinum. The strength of the solution was so adjusted that no immediate precipitation took place. By exposing the dish containing the mixture, to a surface of sulphuric acid for a few hours, the salt was generally procured in fine crystals. In this manner

the platinum-salts of amylamine, œnanthylamine, caprylamine, and pelargonamine were prepared. The second and fourth of these bases are entirely new, and it is believed that none of them have ever before been procured from a homologue of olefiant gas.

I have not, as yet, been able to obtain any iodide of caproyl.

Platinum-salt of Amylamine.

Amylene is present in such small quantity in Boghead naphtha, that only a very minute portion of iodide of amyl could be obtained. I recognised the hydrochlorate at once by its peculiar fatty appearance; and the platinum-salt crystallised in superb scales, exactly resembling the salt which I had often had occasion to prepare by the ordinary processes.

The following numbers were obtained on analyses:—

I.—0·2135 gramme of platinum-salt of amylamine gave 0·0715 gramme of platinum.

II.—0·2004 gramme of platinum-salt of amylamine gave 0·0682 gramme of platinum.

Or, in per centages:—

Experiment.		Mean.	Theory.
I.	II.		
33·48	34·13	33·76	33·76

Platinum-salt of Cœnanthylamine.

I have already shown the presence of œnanthylene in Boghead naphtha.* The quantity of iodide of œnanthyl formed, appears to be exceedingly small, and I was only able to obtain enough platinum-salt for one determination. It consisted of beautiful orange-coloured scales.

0·1186 gramme of platinum-salt of œnanthylamine gave 0·0366 gramme of platinum.

Experiment.	Theory.
30·86	30·79

Platinum-salt of Caprylamine.

The iodide of capryl appears to be formed more readily than its congeners. The crystals of the platinum-salt of the cor-

* Philosophical Transactions, 1858.

362 GREVILLE WILLIAMS ON FORMATION OF IODIDES, ETC.

responding base consisted of beautiful golden scales, some of them a quarter of an inch in diameter. They were soluble in alcohol and ether; the salt was, therefore, washed with a little water and pressed between folds of filtering-paper. Several grammes were prepared with comparative ease.

The following numbers were obtained on analysis:—

I.—0.3432 grm. of platinum-salt of caprylamine gave 0.3616 grm. of carbonic acid, and 0.1906 grm. of water.							
II.—0.2195 grm. of platinum-salt of caprylamine gave 0.0645 grm. of platinum							
III.—0.2084	"	"			0.0614	"	
IV.—0.2028	"	"			0.0596	"	
V.—0.2066	"	"			0.0616	"	
	I.	II.	III.	IV.	V.	Mean.	Calculation.
Carbon	28.73					28.73	C ¹⁶ 96 28.62
Hydrogen	6.17					6.17	H ²⁰ 20 5.96
Nitrogen	. . .					. . . N	14 4.17
Chlorine	. . .					. . . Cl ³	106.5 31.74
Platinum	. . . 29.38	29.46	29.39	29.81	29.51	Pt	99 29.51
							335.5 100.00

The first and fourth analyses were made on the same specimen; the second, third, and fifth upon distinct preparations in each case.

Platinum-salt of Pelargonamine.

The iodide of pelargonyl was formed from Boghead naphtha in sufficient quantity to enable me to attain the hitherto unknown volatile alkaloid, pelargonamine. The crystals of the platinum-salt, although of a rich golden-yellow, were less beautiful than the others, and on drying at 100°C. caked slightly together. They did not, however, become in the least discoloured. The annexed numbers give the results of the analyses—

I.—0.3978 grm. of platinum-salt of pelargonamine gave 0.4474 grm. of carbonic acid, and 0.2304 grm. of water.			
II.—0.1184 grm. of platinum-salt of pelargonamine gave 0.0340 grm. of platinum			
III.—0.2132	"	"	0.0604 "
IV.—0.2364	"	"	0.0678 "

	I.	II.	III.	IV.	Mean.	Calculation.		
Carbon	30·70				30·70	C ¹⁸	108	30·90
Hydrogen	6·44				6·44	H ²²	22	6·30
Nitrogen	...				...	N	14	4·01
Chlorine	...				...	Cl ³	106·5	30·47
Platinum	...	28·71	28·33	28·68	28·57	Pt	99	28·32
							<hr/>	<hr/>
							349·5	100·00

Each platinum-determination was made on a different specimen. I hope, eventually, to submit to the Society several more substances obtained from Boghead naphtha by the agency of hydriodic acid. It is evident that several of the true radicles may now be prepared by acting on the above iodides with sodium.