IX.—*On the Action of Iodide of Ethyl on Toluidine.*

BY REGINALD I. MORLEY AND JOHN S. ABEL,

ASSISTANTS IN THE ROYAL COLLEGE OF CHEMISTRY.

Chemists are acquainted with the results obtained by Dr. Hofmann in his researches on the organic bases, which led him to establish the existence of four groups of bases derived from ammonia, by the replacement of its several hydrogen equivalents by organic radicals. He pointed out at the same time a simple method of ascertaining in what group an organic base has to be classified. This method, as is well known, consists in treating the substance under examination with the iodide of an alcohol radical.

The experiments to which we are about to refer, undertaken at

his invitation, and carried out under his kind superintendence, refer to the examination in this direction of an organic base which has repeatedly claimed the attention of the faculty—viz., Toluidine. The origin of this body, derived step by step from toluylic acid, toluol, and nitrotoluol, places the substance on the same line with the aniline, the formation of which from benzoic acid, benzol, and nitrobenzol is well known. The perfect homology of toluidine and aniline is moreover unequivocally proved by their physical properties. The constitution of aniline has been established, it may be said, beyond any doubt: it has been proved that in its salts the substance may be received as ammonium in which 1 equiv. of hydrogen is replaced by 1 equiv. of the hydrocarbon, $C_{12}H_5$, to which the name of Phenyl has been given, or in the free state as ammonia, 1 equiv. of hydrogen of which is replaced by the same radical.

If toluidine is a perfect homologue of aniline, its constitution must be perfectly similar; so that if the latter has in fact this constitution, toluidine must be represented by the formula

when it becomes ammonia in which 1 equiv. of hydrogen is replaced by toluyl, $C_{14}H_7$; and it is this constitution which has been assumed by Dr. Hofmann in his papers on the bases. It remained to verify this assumption experimentally. This verification forms the subject of the present communication. We rapidly pass over the preparation of toluol from coal naphtha, although we had to perform an immense number of distillations, until the hydrocarbon at last boiled stationary at 111°C . ($231^\circ 8 \text{F}$.) The conversion of toluol into nitrotoluol is attended with difficulties: heat must be carefully avoided, otherwise a considerable quantity of

dinitrotoluol is produced, which forms far more readily than dinitrobenzol. The reduction of nitrotoluol by means of sulphuretted hydrogen, lastly, is an operation tedious in the extreme; it can be accomplished only by a series of supersaturations and distillations. The purification of the toluidine was effected in the form of oxalate. On account of the facility with which it was obtained, we selected from among the alcohol-iodides, iodide of ethyl as the substance to the action of which the toluidine was to be submitted.

We now proceed to describe the results obtained in this reaction.

ETHYLOTOLUIDINE.

A portion of the toluidine was sealed up in a tube with excess of iodide of ethyl, and exposed to the temperature of the water-bath for two or three days. The toluidine mixed with the iodide, and the whole became one crystalline mass; towards the latter part, however, an oily layer separated on the upper surface of the liquid. The tube was now opened, and the excess of iodide of ethyl distilled off in a water-bath, when iodide of ethyltoluidine remained as a heavy oil possessing a peculiar alliaceous smell; this oil was decomposed by distillation with a strong solution of potassa at a high temperature, when a colourless oil distilled over, lighter than water, and possessing a peculiar odour. This oil, the new base, was separated from the water with which it had distilled over, and dried over stick potash. When thus rectified, its boiling point was found to be 217° C. ($422^{\circ}\cdot6$ F.), the spec. grav. being $0\cdot9391$ at $15^{\circ}\cdot5$ C. (60° F.)

From the comparison of the boiling points of aniline, (about 180° C.), and toluidine (200° C.), we might have expected that by the introduction of 4 equivs. of carbon and hydrogen into the latter base, its boiling point would have been raised about 40° C. It appears, however, that this rule does not hold good in all cases of this kind, Dr. Hofmann having observed a similar comportment with ethylaniline.

Platinum-salt of Ethyltoluidine.—This was at first prepared by adding excess of hydrochloric acid to the liquid from which the base had been separated, and which possessed a strong alkaline reaction. The hydrochlorate thus formed was evaporated on a water-bath, until, when mixed with bichloride of platinum, the double salt crystallized on cooling. In this manner a considerable quantity of a fine crystalline salt was obtained, soluble in water, and, when washed with alcohol, of a pale yellow colour. For analysis, a portion of the crystals was

dried in the water bath, until the weight was constant, and burnt as usual. The quantity of platinum obtained was slightly too large for ethyltoluidine; a circumstance which we explained by the possible presence of a trace of toluidine in the liquid from which the salt was prepared.

An attempt to recrystallize the salt only resulted in the total loss of our substance by decomposition; a fresh portion of hydrochlorate was prepared from some of the base, evaporated, and mixed with bichloride of platinum; a precipitate was formed which dissolved in excess of the bichloride, from which solution the salt could not again be obtained. It was necessary, therefore, to add the platinum solution very cautiously, and when the precipitate was formed, alcohol was added, which dissolved the salt, but again deposited it on agitation after a short time. In this manner, with much trouble, sufficient platinum-salt was prepared for another determination. The double salt being very soluble in alcohol, it was washed with ether; it was found to decompose at 100° C. As the colour became darker, and no constant weight could be arrived at, it was dried for analysis *in vacuo* over sulphuric acid.

0.1580 grm. of platinum-salt gave

0.0460 „ platinum = 29.11 per cent.

According to the formula $C_{18}H_{13}N, HCl, PtCl_2$, or

the percentage of platinum should be 28.93 per cent. The difference is 0.08.

Our next step was to confirm the composition of the base by a determination of the carbon and hydrogen. The platinum-salt being so difficult to obtain, we burnt the base itself, which, as it darkens on keeping, like aniline, toluidine, &c., was redistilled for this purpose.

0.1425 grm. of substance gave

0.4175 „ carbonic acid

0.1255 „ water,

leading to the following percentages,

Carbon	.	.	.	79.90
Hydrogen	.	.	.	9.78

The formula

requires the following values :

	Theory.	Experiment.
18 equivs. of carbon . . .	108 = 80.00	79.90
13 „ hydrogen . . .	13 = 9.63	9.78
1 „ nitrogen . . .	14 = 10.37	
	<hr/> 135	<hr/> 100.00

These numbers sufficiently establish the composition of ethylotoluidine. Ethylotoluidine forms crystalline compounds with oxalic and sulphuric acids.

DIETHYLOTOLUIDINE.

A portion of the ethyl-base was next sealed up with an excess of iodide of ethyl, and exposed for two or three days to the temperature of boiling water, in order to produce diethylotoluidine. After that time, on allowing the tube to cool and gently agitating it, beautiful crystals of the iodide of the new base at once formed throughout the whole length of the liquid, which dissolved again on placing the tube in the water bath. The excess of iodide of ethyl was again separated as before, when the iodide of diethylotoluidine remained in the flask, from which it crystallized in fine six-sided prisms, so soluble in water that they could scarcely be crystallized from it. The salt separated from the aqueous solution in oily drops, which assumed the crystalline form on being touched with a glass rod. It appeared to be decomposed by alcohol, as also by continued exposure to the atmosphere. For analysis, some of the recrystallized salt was dried *in vacuo* over sulphuric acid (the crystals having been found to decompose in the water bath), dissolved in water, and the iodine determined by precipitation with nitrate of silver in the usual manner.

0.3130 grm. of iodide gave

0.2520 „ iodide of silver,

corresponding to percentage of iodine, 43.45. The formula

requires 43·66 per cent. of iodine ; thus proving the crystals to have the above composition.

The remainder of the salt was distilled with potash, and the base thus obtained on the surface of water, from which it was separated. Diethyltoluidine is colourless, and possesses a smell like the former compound. After rectification from potash it was found to boil at 229° C. (444°·2 F.), thus showing another deviation from the rule. Its spec. grav. at 15°·5 C. (60° F.) was 0·9242.

The preparation of the platinum-salt of this base presented insurmountable difficulties : it could not be obtained otherwise than as a resinous mass, to crystallize which all attempts were abortive.

A combustion of the base was however made :

0·1495	gram.	of substance	gave
0·4435	„	carbonic acid,	
0·1410	„	water,	

leading to the following percentages :

Carbon	.	.	.	.	80·90
Hydrogen	.	.	.	.	10·47

The formula

requires the following values :

		Theory.		Experiment.
22 equivs. of carbon	.	132	80·98	80·90
17 „ hydrogen	.	17	10·43	10·47
1 „ nitrogen	.	14	8·59	
		163	100·00	

The results obtained correspond therefore sufficiently with the above formulæ.

OXIDE OF TRIETHYLOTOLUYLAMMONIUM.

It now remained for us to convert the volatile into a fixed base, similar to those which Dr. Hofmann has distinguished by the laboratory term ammonium-bases. The formation of such a substance by the introduction of another equivalent of $\text{C}_4 \text{H}_5$ into diethyltoluidine would establish beyond any doubt the perfect homology of aniline and toluidine.

This new base might be called oxide of triethyltoluidine or oxide of triethyltoluylammonium.

For this purpose we again sealed up the last base with iodide of ethyl, and exposed the tube to a temperature of 100°C . (212°F .) for some days, till fine prismatic crystals of an iodide had formed in the solution. After distilling off the excess of iodide of ethyl as before, the iodide of the new base remained as a heavy oil: this was decomposed by heating with freshly precipitated oxide of silver, when the liberated oxide of triethyltoluylammonium at once entered into solution, leaving iodide of silver. The solution after filtration was found to possess an extremely bitter taste, and to be very alkaline to test-paper. With salts of the metallic oxides, a solution of this base behaved in most cases similarly to potash and to Dr. Hofmann's oxide of tetrethylammonium: thus, with salts of baryta, strontia, lime, and magnesia, a white precipitate insoluble in excess was formed.

The following is a list of the reactions of this substance:

Barium-salts.—White precipitate of the hydrate of the earth, insoluble in an excess of the base.

Strontium-salts.—White precipitate of the hydrate of the earth, insoluble in an excess of the base.

Calcium-salts.—White precipitate of hydrate of the earth, insoluble in excess of the base.

Magnesium-salts.—White precipitate of hydrate of the earth, insoluble in an excess of the base.

Aluminum-salts.—White gelatinous precipitate soluble in large excess of the base.

Chromium-salts.—Green hydrated sesquioxide insoluble in excess.

Nickel-salts.—Green protoxide insoluble in excess.

Cobalt-salts.—Pink hydrate of protoxide insoluble in excess.

Manganese-salts.—Whitish hydrated protoxide insoluble in excess.

Salts of Protoxide of Iron.—Green hydrated protoxide insoluble in excess.

Salts of Sesquioxide of Iron.—Brown hydrated sesquioxide insoluble in excess.

Zinc-salts.—Hydrate of the protoxide soluble in excess.

Lead-salts.—White hydrate of protoxide soluble in excess.

Silver-salts.—Brown protoxide insoluble in excess.

Salts of Suboxide of Mercury.—Black suboxide insoluble in excess.

Salts of Protoxide of Mercury.—White precipitate insoluble in excess.

Copper-salts.—Blue hydrated protoxide insoluble in excess, becoming black by ebullition.

Cadmium-salts.—White hydrated protoxide insoluble in excess.

Bismuth-salts.—White hydrated teroxide insoluble in excess.

Antimony-salts, Teroxide.—White hydrated teroxide soluble in excess.

Salts of Protoxide of Tin.—White hydrated protoxide soluble in excess.

Salt of Bin oxide of Tin.—White hydrated bin oxide soluble in excess.

Gold-salts.—Yellow precipitate of the double salt.

Platinum-salts.—Yellow precipitate of the double salt.

Platinum-Salt.—When the chloride of this base was mixed with bichloride of platinum, a copious precipitate of a fine crystalline platinum-salt was produced, which was nearly insoluble in cold water, but was dissolved readily in hot water, from which solution it crystallized in beautiful needles.

The salt was thrown upon a filter, washed and dried at 100° C.

Both the original and crystallized salts were analyzed.

- I. 0.1640 grm. of platinum-salt gave on ignition
0.0410 „ platinum.
- II. 0.6100 grm. of platinum-salt gave on ignition
0.1515 „ platinum.

	Theoretical percentage.	Experimental percentage.
Platinum . . .	24.85	24.91

Recrystallized salt.

- 0.5212 grm. of platinum-salt gave on ignition
- 0.1292 „ platinum.

	Theory.	Experiment.
Platinum . . .	24.85	24.5

It appears, therefore, that this platinum-salt, like some observed by Dr. Hofmann, loses platinum by recrystallization.

For combustion, some of the original salt was employed.

0·5300 grm. of platinum-salt gave
 0·7600 „ carbonic acid,
 0·2690 „ water, and
 0·1310 „ platinum.

The numbers required by the formula

are shown in the following table, together with the numbers obtained by experiment, from which it will be seen that little doubt can remain as to the formula of the salt analyzed.

			Theory.		Experiment.
26 equivs. of carbon			156	39·27	39·11
22 „	hydrogen		22	5·54	5·64
1 „	nitrogen		14	3·52	
1 „	platinum		98·7	24·85	24·71
3 „	chlorine		106·5	26·82	
			397·2	100 00	

These experiments establish the existence of the following bases, which we place in juxtaposition with those of the homologue phenyl.

Phenylamine	$\left. \begin{array}{l} \text{H} \\ \text{H} \end{array} \right\} \text{N}$	Toluyamine	$\left. \begin{array}{l} \text{H} \\ \text{H} \end{array} \right\} \text{N}$
Aniline	$\text{C}_{12} \text{H}_5 \left. \vphantom{\begin{array}{l} \text{H} \\ \text{H} \end{array}} \right\} \text{N}$	Toluidine	$\text{C}_{14} \text{H}_7 \left. \vphantom{\begin{array}{l} \text{H} \\ \text{H} \end{array}} \right\} \text{N}$
Ethylaniline	$\left. \begin{array}{l} \text{H} \\ \text{C}_4 \text{H}_5 \\ \text{C}_{12} \text{H}_5 \end{array} \right\} \text{N}$	Ethyltoluidine	$\left. \begin{array}{l} \text{H} \\ \text{C}_4 \text{H}_5 \\ \text{C}_{14} \text{H}_7 \end{array} \right\} \text{N}$
Diethylaniline	$\left. \begin{array}{l} \text{C}_4 \text{H}_5 \\ \text{C}_4 \text{H}_5 \\ \text{C}_{12} \text{H}_5 \end{array} \right\} \text{N}$	Diethyltoluidine	$\left. \begin{array}{l} \text{C}_4 \text{H}_5 \\ \text{C}_4 \text{H}_5 \\ \text{C}_{14} \text{H}_7 \end{array} \right\} \text{N}$
Triethylaniline	$\left. \begin{array}{l} \text{C}_4 \text{H}_5 \\ \text{C}_4 \text{H}_5 \\ \text{C}_4 \text{H}_5 \\ \text{C}_{12} \text{H}_5 \end{array} \right\} \text{N}$	Triethyltoluidine	$\left. \begin{array}{l} \text{C}_4 \text{H}_5 \\ \text{C}_4 \text{H}_5 \\ \text{C}_4 \text{H}_5 \\ \text{C}_{14} \text{H}_7 \end{array} \right\} \text{N}$

In conclusion, we may observe that the combustion of this pla-

tinum-salt, as well as all the combustions made in the course of this investigation, were performed in Dr. Hofmann's new gas furnace for organic analysis. It deserves to be mentioned, that to ensure complete combustion, the liquids were weighed in small open tubes filled with oxide of copper and a little powdered chlorate of potassa, the oxygen of which, expelled with the last stage of the process, ensured the complete combustion of any small particles of carbon that might otherwise have remained unconsumed.