XVIII.—*On the Action of Chloride of Cyanogen upon Toluidine.**By W. WILSON,*

The perfect homology existing between toluidine and aniline left but little doubt respecting the deportment which the former alkalioid would exhibit, when exposed to the influence of chloride of cyanogen; still the discrepancies which we frequently observe between the various members of one series, especially if we rise on the scale of compounds, made it desirable to establish the behaviour of toluidine by experiment.

PREPARATION OF TOLUIDINE.

The preparation of toluidine is a process of considerable difficulty, inasmuch as the collateral hydrocarbon can be obtained only in comparatively small quantities. The formation of toluol has hitherto been observed in different processes, namely: in the distillation of tolu-balsam by Deville, its discoverer; in the distillation of dragon's blood (dracyl), by Boudault and Glenard; in the decomposition of toluyllic acid by Noad; and lastly it has been met with among the hydrocarbons of coal-tar naphtha by Mansfield.

I have tried all these methods in order to procure toluol in larger quantities, and I find that the source last-mentioned is that which yields this compound most easily and in greatest quantity;—only comparatively minute quantities being obtained by the other processes.

The best plan is to select the fraction distilling between 100° and 120° C., and to treat this portion with half its bulk of concentrated sulphuric acid. I am not prepared to say what substances are removed by this process; the fact is, however, that a constant boiling-point is more easily reached with, than without, the use of

sulphuric acid. In all cases, a series of tedious distillations is required, in order to accomplish this object. The boiling-point of toluol was found to be 110° C.

The conversion of toluol into nitro-toluol succeeds without difficulty in the usual manner. Nitro-toluol was found to boil between 220° and 225° , without decomposition.

Those chemists who have used Zinins' process for the amidation of nitro-compounds, are aware how difficult it is to effect the complete conversion of these substances when treated with sulphide of ammonium, especially if there is but 1 equivalent of hyponitric acid present. I have used in my experiments a solution of hydrosulphate of sulphide of potassium with which the nitro-toluol was repeatedly distilled. The advantages which the potassium-compound presents are very remarkable, not half the time being required as with sulphide of ammonium; moreover, the base, once formed, has no longer to be separated from the ammonia which, in the latter case, distils over with it.

The toluidine obtained in this manner, after having been several times crystallized, in the form of oxalate, and lastly, distilled with caustic lime, presents all the properties which its discoverers assigned to it.

PREPARATION AND ANALYSIS OF METOLUIDINE.

In subjecting toluidine to the action of chloride of cyanogen. I adopted, in the first place, the same arrangement that Dr. Hofmann had used in preparing melaniline, namely, a series of tubes, filled with the *dry* alkaloid, through which the chloride of cyanogen was drawn by means of an aspirator. I soon found, however, that the deportment of toluidine is by no means so simple as that of aniline under similar circumstances. The alkaloid being solid at ordinary temperatures, it was necessary to support the action from the very commencement by the application of heat, under the influence of which, unless it be very carefully applied, the newly formed hydrochlorate appears to undergo some farther metamorphoses. On this account I found it more convenient to introduce toluidine into a slightly bent tube, to diffuse it by a gentle heat into a thin layer over the sides, and then to expose this increased surface to the action of the gas. In this manner the heat evolved during the reaction was sufficient to keep the substance in a state of fusion. As soon as the action had ceased, the resinous mass, consisting almost entirely of hydrochlorate of the new base, was dissolved in water to which a small quantity

of hydrochloric acid had been added. On mixing the filtered solution with potassa, a white precipitate took place which was boiled for some time with the potassa, in order to distil off with the aqueous vapours small quantities of toluidine which might have escaped the action. The residue was thrown upon a filter, separated by washing, from the chloride of potassium, and recrystallized from alcohol.

From this solution, the new base, which I propose to call *Metoluidine*, a name corresponding to melaniline, is deposited in small crystalline plates. It crystallizes better from a mixture of alcohol and water, but by no means with the same facility as melaniline; this substance is but slightly soluble in water, but somewhat more so at the boiling-temperature.

I have established the composition of metoluidine by analyses of the base itself, and by that of the platinum-salt:

0.2201 grm. of base gave
0.6048 „ of carbon, and
0.1454 „ of water.

These numbers, together with those obtained with the platinum-salt, lead to the formula

which requires the following values:

	Theory.		Experiment.
30 equivs. of Carbon . . .	180	75.31	74.54
17 „ „ Hydrogen . . .	17	7.11	7.34
3 „ „ Nitrogen . . .	42	17.58	—
	<hr/> 239	<hr/> 100.00	

METOLUIDINE AND BICHLORIDE OF PLATINUM.

Metoluidine is readily soluble in hydrochloric acid. The solution yields, with bichloride of platinum, a dark-yellow precipitate, which is insoluble in water and alcohol, and may be dried at 100°.

On analysis, the following numbers were obtained:

- I. 0.2685 grm. of platinum-salt gave:
0.3980 „ „ carbonic acid, and
0.1025 „ „ water.
- II. 0.1897 „ „ platinum-salt gave:
0.0418 „ „ platinum.
- III. 0.2985 „ „ platinum-salt gave:
0.0659 „ „ platinum.
- IV. 0.1096 „ „ platinum-salt gave:
0.0244 „ „ platinum.

These numbers lead to the following percentage-composition :

	I.	II.	III.	IV.
Carbon . .	40·40	—	—	—
Hydrogen . .	4·04	—	—	—
Platinum . .	—	22·03	22·07	22·25

The formula

requires the following values :

	Theory.		Experiment.
30 equivs. of Carbon . . .	180·00	40·43	40·40
18 „ „ Hydrogen . .	18·00	4·04	4·24
3 „ „ Nitrogen . .	42·00	9·43	—
3 „ „ Chlorine . .	106·50	20·93	—
1 equiv. „ Platinum . .	98·68	22·17	22·15
1 „ „ „ Platinum-salt .	445·18	100·00	

The formation of metoluidine is perfectly analogous to that of melaniline; 2 equivalents of toluidine, and 1 equivalent of chloride of cyanogen, yield 1 equivalent of hydrochlorate of metoluidine.

* The bases produced by the action of chloride of cyanogen upon aniline and toluidine, exhibit a remarkable analogy with one of the platinum alkaloids obtained by M. Reiset, which will at once become perceptible if we compare the formula of the chlorides, when considered as ammonia compounds :