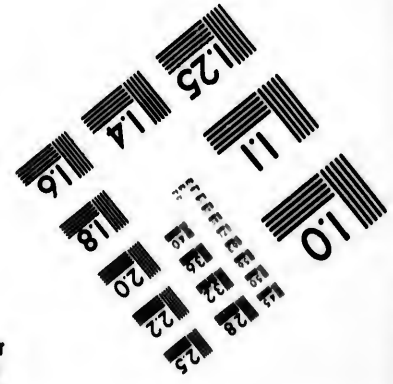
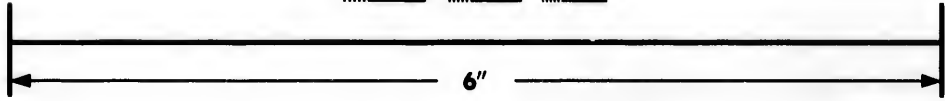
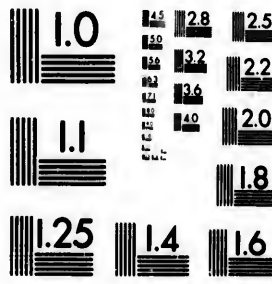


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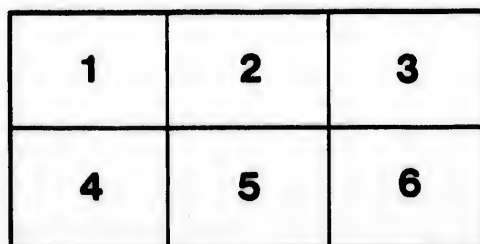
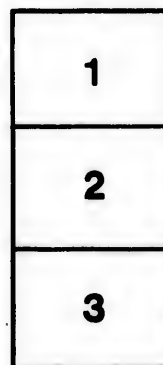
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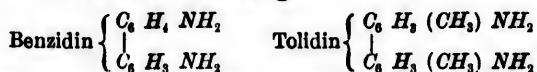
[Reprinted from THE CANADIAN RECORD OF SCIENCE, October, 1889.]

### DERIVATIVES OF TOLIDIN.

R. F. RUTAN, B.A., M.D.

In 1845 a Russian chemist named Zinin,<sup>2</sup> by reducing Azobenzol with hydrogen sulphide obtained a substance which, when further treated with sulphuric acid gave rise to a base called Benzidin. The intermediate product of the reduction of azobenzol was subsequently examined by Hofmann<sup>3</sup> and found to be Hydrazobenzol, and the nature of the reaction giving rise to Benzidin was made clear.

From a homologue of hydrazobenzol, viz. : hydrazotoluol by Hofmann's method, Petriew<sup>4</sup> prepared the homologue of Benzidin, viz., Tolidin, and studied some of its characteristics. The constitution of both Benzidin and Tolidin was afterwards established by Gustav Schultz.<sup>5</sup> These two bases were shown by him to be double molecules of anilin and toluidin, respectively, connected by their benzol neuclei, and having their amidogen groups in the para position. Their formulae being:—



Benzidin has received some attention from chemists and many of its reactions have been investigated. Tolidin, on the other hand, owing to the difficulty with which it was

<sup>1</sup> In a former communication to this journal, they were referred to as probably at the top of Div. 2. (See July, 1889.)

<sup>2</sup> Journal für praktische Chemie, xxxvi., 93.

<sup>3</sup> Jahrsbuicht der Chemie, 1863, 424.

<sup>4</sup> Berichte, vi., 557.

<sup>5</sup> Liebigs Annalen, 174, 227. Berichte, xvii., 467.

obtained, and its apparent unimportance, has received until lately no attention whatever. These two bases were long regarded merely as chemical curiosities whose chemical relations were of importance only so far as their existence threw light on other reactions, and thus aided generalization. A few years ago, however, Greiss<sup>1</sup> announced that benzidin, like anilin, formed a diazo compound on treatment with nitrous acid. From this Gustav Schultz, of Berlin, in 1879, prepared the first of the now important class of dyes called Azo-dyes from Benzidin, but the first economic dye of this class was patented in 1884 and named Congo red. These dyes, now very numerous, owe their importance in the arts to the fact that they dye wood and cotton fibre directly, *i.e.*, without the use of a mordant.

The success of the Congo red and other dyes of this class lead to the preparation of these rare bases, Benzidin and Tolidin, in available quantity. Through the kindness of Prof. Hofmann I was enabled to obtain from Gustav Schultz, of the Berlin anilin factory, a kilogramme of crude Tolidin, and began the study of its derivatives in Berlin three years ago. Some of these compounds have already been described by me, and formed part of a paper read before the British Association in 1886,<sup>2</sup> but others have been obtained since. This paper deals chiefly with those derivatives obtained directly from the base Tolidin, and includes only those secondary derivatives necessary to illustrate completely a particularly reaction of the base itself. The subject is, however, by no means worked out as in a direction indicated at the end of this paper, it gives promise of interesting results yet to be obtained.

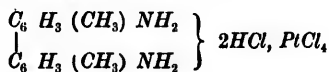
The crude base obtained from the factory proved to be the ortho-tolidin, and on purification crystallized in glistening scales of a pale violet hue, melting at 128° C—not at 112°, as was originally stated by Petriew.<sup>3</sup> It turns intensely blue when treated with oxidizing agents, gives a

<sup>1</sup> Journal für praktische Chemie, 101, 92.

<sup>2</sup> Proc. Brit. Ass'n., 1886.

<sup>3</sup> Loc cit.

blue color with ferric chloride when concentrated, and green when dilute, when boiled this turns red and gives a precipitate of ferric hydrate. The sulphate is very insoluble; the hydro-chlorate is soluble in water and in alcohol; it forms with Platinum chloride beautiful yellow acicular crystals, usually in rosettes, insoluble in water and dilute alcohol. These decompose on exposure to moist air, but if dried after precipitation by washing with alcohol and ether, they may be further dried at 100° and analysed. The following results confirm the formula:—



Calculated.

Platinum = 31.07 per cent.

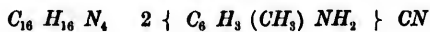
Found.  
I. II.  
30.81. 30.90.

Cyanide of Tolidin.

Cyanogen gas, evolved by heating mercuric cyanide, was slowly passed through a cold saturated alcoholic solution of Tolidin, till a distinct precipitate occurred, the solution was tightly corked and allowed to stand for forty-eight hours.

A voluminous, brown, amorphous precipitate resulted, which, when filtered and washed with alcohol, ether and benzol, was dried and examined. This product was found to be a reddish brown amorphous body, insoluble in water, alcohol, ether or benzol, very slightly soluble in phenol, ligroin and nitro benzol. It did not melt at 320°, and burned with difficulty when heated on platinum. It decomposed into tolidin and oxalic acid when heated with acids.

In making the combustion of this substance it was found necessary to add lead chromate to the copper oxide to ensure complete oxidation, and even then the combustion was very tedious. The following figures established the formula:—



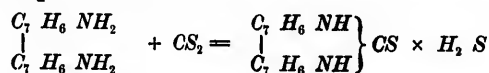
Theory.

Found.

	I.	II.	III.
C = 72.72	71.96	71.8	....
H = 6.06	6.11	6.21	....
N = 21.21	....	....	21.43

*The Thio-urea.*

Twenty grammes of Tolidin in alcohol were boiled with an equal weight of carbon bisulphide in a flask with reversed condenser for six hours. The result was the formation of a white crystalline powder, melting at 185° and insoluble in most media, but soluble in strong sulphuric acid, from which it was precipitated on dilution. Hydrogen sulphide was evolved during the reaction. The resulting compound had the formula:  $C_{14}H_{14}N_2CS$ , and the reaction which occurred may be represented thus:



The following are the analytical results:—

Theory.	Found.		
	I.	II.	III.
C = 70.86 per cent.	71.11	71.06	....
H = 5.50 "	6.03	5.81	....
N = 11.02 "	....	....	....
S = 12.01 "	....	....	12.14

All attempts to convert this into an iso-sulpho-cyanide by the usual methods were ineffectual.

*Diacetyl Tolidin.*

Tolidin, when boiled for a few hours with 7-8 times its weight of glacial acetic acid, in a flask with reversed condenser, readily forms the diacetyl tolidin. The same substance is at once formed in the cold when acetic anhydride is added to a solution of the base. It is a white crystalline powder, melting above 320° and insoluble in the usual solvents. It is deposited, however, in snow white needles on cooling its solution in boiling nitro-benzol; when thus purified and dried at 130° it yielded the following analytical data:—

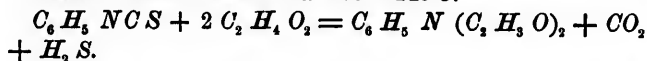
Calculated for  $C_{18}H_{20}N_2O_2$

Theory.	Found.		
	I.	II.	III.
C = 72.97	72.62	72.29	....
H = 6.75	6.88	6.59	....
N = 9.46	....	....	9.75
O = 10.81	....	....	....



*Tetra-acetyl Tolidin.*

This is probably the most interesting of all the derivations of Tolidin, inasmuch as it is, with one exception, the only example of a primary base in which both of the hydrogen atoms in the amidogen group ( $NH_2$ ) have been replaced by the acetyl radicle. The only other compound of this class is Diacetanilid.\*  $C_6 H_5 N (C_2 H_3 O)_2$ . Hofmann prepared this by the action of glacial acetic acid on phenyl mustard oil in a sealed tube at  $130^\circ-140^\circ C$ .

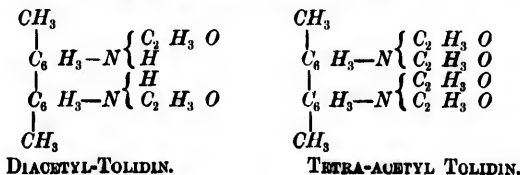


From the readiness with which the acetyl radicle united with the tolidin it was supposed that a similar compound might be obtained directly by treating diacetyl tolidin with acetic anhydride. Accordingly diacetyl tolidin was, with 6-7 times its weight of acetic anhydride sealed in tubes and submitted to a temperature of  $180^\circ C$  for six hours. The tubes were then found to contain in a dark fluid acicular crystals, which were soluble in alcohol, ether, benzol and acetic acid, but insoluble in water. After purification, the substance was found to crystallize in long, silky, snow white needles, melting at  $210^\circ$  and on analysis gave the following results:—

Calculated for  $C_{22} H_{24} N_2 O_4$

<i>Theory.</i>	<i>Found.</i>	
	I.	II.
$C = 69.47$	69.28	....
$H = 6.32$	6.61	....
$N = 7.37$	....	7.65
$O = 16.84$	....	....

When treated with dilute alkalis it at once broke down into diacetyl tolidin and acetic acid. The two acetyl derivations of Tolidin may be thus represented:—



*Dinitio-diaetyl-tolidin.*

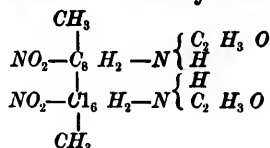
Diaetyl tolidin is easily nitrated when added in small quantities to fuming nitric acid, and the violence of the reaction moderated by surrounding the flask with ice cold water and maintaining a large excess of nitric acid. The mixture is then poured into a long beaker filled with snow and the precipitated nitro body filtered and washed. It is insoluble in alcohol, water and the usual media, but may be, like diaetyl tolidin, purified by precipitation from solution in boiling nitro benzol. This compound, at first of a brown tint, can be obtained almost white by repeated re-crystallization. It does not melt, and when an attempt was made to purify by sublimation it exploded violently.

On combustion it yielded the following data:—

Calculated for  $C_{18} H_{18} N_4 O_6$

<i>Theory.</i>	<i>Found.</i>	
C = 55.96	55.73	....
H = 4.66	4.82	....
N = 14.51	....	15.10
O = 24.87	....	....

These results are in conformity with the formula:—

*Dinitro-tolidin.*

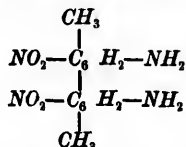
When the body above described is saponified by prolonged boiling with strong caustic potash a red compound results, which from a large volume of boiling dilute alcohol may be obtained in garnet red tabular crystals which melt at 265° and explode on heating to a higher temperature. It is with difficulty dissolved in any ordinary solvent.

It yielded on analysis the following results:—

Calculated for  $C_{14} H_{14} N_4 O_4$

<i>Theory.</i>	<i>Found.</i>	
	I.	II.
C = 55.63	55.87	....
H = 4.65	4.91	....
N = 18.54	....	18.10
O = 21.16	....	....

This points to the following as the probable formula :—



It was thought probable that this compound like other nitro derivatives of the aromatic series might be reduced and a tetra-amido derivative thus obtained but this reduction could not be effected. When dinito tolidin is submitted to the reducing action of nascent hydrogen, evolved either from tin and hydrochloric acid or from sodium amalgam, it breaks down into tolidin, and by no means employed could the nitro groups be reduced to amidogen.

*(Continued.)*

CHEMICAL LABORATORY,  
 McGill Univ., Med. Faculty. }  
 October, 1889.

