PRELIMINARY NOTICE UPON THE ACTION OF BENZALDEHYDE ON COMMERCIAL XYLIDINE.

BY JAMES H. STEBBINS, JR.

This investigation was undertaken with the object, if possible of producing new substances homologous with diamidotriphenylmethan.

O. Fisher (*Ber. d. Chem. Gesell.*, 1879, p. 1693; 1880, p. 667: 1882, p. 676; *Anal. Ch.*, 1881, 206, p. 147) has shown in his elaborate experiments, that diamidotriphenylmethan may easily be produced by the action of benzaldehyde upon aniline chloride or sulphate, in the presence of a dehydrating medium, as for example, zinc chloride. I have availed myself of this reaction, only substituting commercial xylidine for the aniline and using an excess of fuming hydrochloric acid in lieu of zinc chloride.

Now as commercial xylidine is presumably a mixture of ortho- and paraxylidine, it seemed probable that the above reaction would yield a mixture of ortho- and paradiamidodixylylphenylmethan. The following experiments, I think, confirm this expectation:

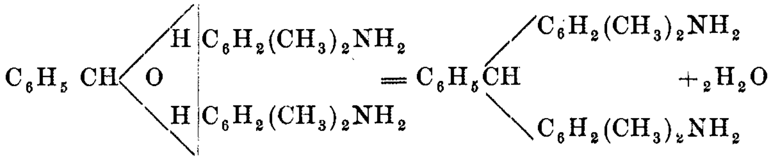
One mol. of benzaldehyde (53 grms.) was heated under return cooler with 2 mols. (121 grms.) of commercial xylidine, and about 3 mols. of fuming hydrochloric acid.

Upon adding the xylidine to the benzaldehyde, prior to the treatment with HCl, the mixture became very hot and small drops of water were formed on the cool, upper sides of the flask. This phenomenon suggested that some sort of condensation had taken place, the nature of which will be further investigated. Disregarding this preliminary reaction, the hydrochloric acid was now added, and the mixture heated to boiling for about six hours, and then poured into cold water. This causes a yellow, gummy mass to separate, which upon stirring, clots together and settles to the bottom of the beaker. When cold, the supernatant fluid was removed by decantation, and the residue washed with cold water.

It was then transferred to a flask and treated with a strong current of steam, in order to drive off any remaining benzaldehyde, allowed to cool and separated from all water by decantation. The now hard and brittle mass was extracted with boiling, dilute hydrochloric acid, in which nearly all is soluble, allowed to cool, filtered in order to separate a small amount of resinous substance, and then heated with an excess of ammonia, which precipitates a basic body in the shape of a faintly yellow-colored curd. The latter was collected on a filter, washed with water till free from NH_4Cl, and dried upon filter paper. It is readily soluble in alcohol, ether, benzine and amyl alcohol, but could not be obtained from any of these solvents in a crystalline form. Its chloride, sulphate, oxalate and picrate are easily soluble in water, particularly so the chloride, but none of these salts could be obtained in a crystalline form.

If platinum chloride be added to an aqueous solution of the chloride, a yellow precipitate is formed, which probably constitutes the platinum double salt. It is only sparingly soluble in hot water, but more so in hot alcohol, from which, on cooling, it separates in yellow flakes again, and, on exposure to the air, turns green. If a sample of the base be heated for a short time with strong HNO_3, and then poured into cold water, a copious, yellow, floculent precipitate separates, which probably constitutes a nitro-compound.

Not having any analytical data at hand, I cannot with certainty form any conclusions as to the exact composition of the new base, but, judging from its mode of formation, it may possibly have the following composition :



$$C_6H_5\ CH\left\langle\begin{matrix}H \\ O \\ H\end{matrix}\right.\left|\begin{matrix}C_6H_2(CH_3)_2NH_2 \\ \\ C_6H_2(CH_3)_2NH_2\end{matrix}\right. = C_6H_5CH\left\langle\begin{matrix}C_6H_2(CH_3)_2NH_2 \\ \\ C_6H_2(CH_3)_2NH_2\end{matrix}\right. + {}_2H_2O$$

A compound of this kind might be called diamidodixylylphenylmethan, and so I will continue to call it, until better informed as to its constitution. If it is constituted as above, by replacing the hydrogen atoms of the NH_2 groups with alcoholic radicals, we might expect to obtain a compound similar in nature to the leuco-base of malachite green, which, upon oxidation, would yield the true coloring matter or carbinole.

In order to settle this question, I heated one mol. of the above base, with four mols. of ethyl iodide dissolved in absolute ethyl alcohol, in a sealed glass tube, for three hours, at a temperature of 150° C. The contents of the tube before opening appeared in two layers; the lower one being dark and oily, and the upper one transparent. The tube opened with considerable pressure.

The contents were dissolved in alcohol, and treated with an excess of $NaOH+aq$, which threw down a dark, gummy base, which upon cooling, became much harder, and on exposure to the air turned reddish. It was dissolved in oxalic acid, filtered and concentrated to a syrup, which, on standing, solidifies to a mass of minute, indistinct crystals.

The free base is easily soluble in most of the acids, also in ether, alcohol and benzine. If a solution of the sulphate, together with a little free sulphuric acid be heated with lead peroxide, $PbSO_4$ separates, and the solution turns green, showing beyond much doubt that ethyl radicals have been introduced into the amido-groups. As to the exact number of ethyl groups, I am at present not prepared to say, but presume that as in the case of malachite green, a tetraethyldiamidodixylylphenylmethan was formed, which, upon oxidation, would undoubtedly be converted into the corresponding carbinol, and constitute the above mentioned green coloring matter.

The aqueous solution decanted from the crude diamidodixylylphenylmethan, obtained as previously mentioned, was treated with an excess of ammonia, which threw down a copious yellow-colored gummy mass. After the latter had settled to the bottom of the beaker, the water was decanted and the residue then thoroughly washed with cold water. It was then redissolved in dilute hydrochloric acid, in which it is extremely soluble, and reprecipitated with ammonia, in the shape of a slightly yellow-colored curd. The latter was collected on a filter and washed till perfectly free from NH_4Cl and finally dried on blotting paper.

The base is thus obtained in the shape of a light yellow powder, which is easily soluble in alcohol, ether, amyl alcohol and benzine, and dissolves also very freely in HCl and H_2SO_4, forming salts, which, however, could not be obtained in a crystalline state.

This base differs from the preceding compound in its much greater solubility in acids, and for this reason : ·I am inclined to think that it is an isomer of the first one and possibly may be the diamido-*o*-dixylylphenlymethan, while the former may be the diamido-*p*-dixylylphenlymethan. This, I think, is a fair assumption, inasmuch as I started with commercial xylidine, which is a mixture of the ortho- and para-compounds, and it is to be supposed that in the subsequent treatment with benzaldehyde, they may have both been converted into the corresponding diamidodixylylphenylmethans.

Having at present no analytical data at hand, I am unable to prove the soundness of the above assumptions, but hope in a future paper to present the necessary data, and to throw more light on these interesting compounds.

ABSTRACTS.

GENERAL AND INORGANIC CHEMISTRY.

Contributions to the Study of the Salts of Platinum. E. TROST.

The author does not believe in the equi-saturating power of all oxides, and thinks that the molecules of oxides that enter into the composition of basic salts do not answer to the excess of energy of the base compared with the anhydride. He asks, are not the so-called basic salts the true normal salts?

To study this question he takes the salts of platinum. The accepted formula $Pt(SO_4)_2$; $Pt\ (AsO_3)_4$, $Pt\ SO_3$ are imaginary; he finds that the obtainable platinum salts have a well defined basic character.

1. *Platinum Nitrate.*—The evaporation of the hydrate in strong nitric acid gives a solid body, reddish, insoluble in water and answering to the formula $Pt(N_2O_2)_2\ 3PtO_2\ 5H_2O$. The addition of water to the primitive acid solution gives an hydrate $PtO_2, 3H_2O$, and another $Pt_3O_4 9H_2O$.

2. *Platinic Perchlorate.*—The solution of hydrate platinum in perchloric acid evaporated *in vacuo* gives a basic salt, very different from the normal $Pt(ClO_4)_4$; the salt analyzed was found to be $Pt_6ClO_9, 15H_2O$.