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XXIX.—A Quantitative Study of the Interaction of Glucose and Phenylhydrazine.

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In the course of an investigation, we had occasion to prepare phenylglucosazone from the products of hydrolysis of cellulose. As no references could be found relating to the quantitative nature of this reaction, and as the yield of osazone prepared from pure glucose was found to be very low, an attempt was made to examine the reaction quantitatively.

E. Fischer (*Ber.*, 1884, **17**, 579) noted that the yield of osazone prepared from glucose amounted to 45 per cent. of the theoretical and Ost (*Ber.*, 1913, **46**, 2995) recorded a yield of 50 per cent. of the theoretical from the products of hydrolysis of cellulose. In a more recent paper on the hydrolysis of cellulose by dilute mineral acid by Wohl and Blumrich (*Z. angew. Chem.*, 1921, **34**, 18),

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the yield of glucosazone represented only 27 per cent. of the amount of glucose determined by other methods.

According to E. Fischer (*Ber.*, 1887, **20**, 821), the formation of phenylglucosazone by the interaction of phenylhydrazine acetate and glucose takes place in such a manner that part of the phenylhydrazine acts as an oxidising agent, converting a secondary alcohol group adjacent to the hydrazine group in glucosephenylhydrazone into a ketone group, which combines with a further molecule of phenylhydrazine. That phenylhydrazine should be reduced under these conditions to aniline and ammonia appears remarkable, seeing that its general characteristics are those of a strong reducing agent. Furthermore, phenylhydrazine is not reduced by such a powerful reducing agent as titanous chloride, although in the case of p-nitrophenylhydrazine reduction by this reagent has been shown to take place quantitatively to p-phenylenediamine and ammonia (Robinson, J. Manchester Coll. Techn., 1913, 7, 105).

For the present work, phenylglucosazone was prepared by the interaction of glucose and phenylhydrazine acetate in quantities represented empirically by the equation

$$C_6 H_{12} O_6 + 3 \mathrm{NHPh} \cdot \mathrm{NH}_2 = \mathrm{C}_6 \mathrm{H}_{10} \mathrm{O}_4 (\mathrm{:} \mathrm{N} \cdot \mathrm{NHPh})_2 + \mathrm{NH}_2 \mathrm{Ph} + \mathrm{NH}_3 \\ + 2 \mathrm{H}_2 \mathrm{O},$$

and it was found that 1.8 grams of glucose in 100 c.c. of reacting solution gave, after three hours' heating on a water-bath, yields of osazone amounting to only 50—65 per cent. of the theoretical. Fischer (*loc. cit.*) stated that both aniline and ammonia were formed during the reaction in considerable quantity, but as no quantitative examination appears to have been carried out, an attempt has now been made to examine the filtrate from the osazone preparation for aniline, ammonia, phenylhydrazine, and glucose. This examination was, however, beset with many difficulties, the presence of both glucose and phenylhydrazine rendering copper-reduction methods impracticable, whereas the ordinary methods of estimating aniline have been found useless in presence of phenylhydrazine. If the latter is destroyed by boiling with Fehling's solution, the copper interferes with the aniline estimation.

The action of nitrous acid on phenylhydrazine was examined with a view to its possible utilisation for estimating both aniline and excess phenylhydrazine, for it had been shown by Fischer (Annalen, 1878, **190**, 92) and by Dimroth (Ber., 1902, **35**, 1032) that nitrous acid reacts with phenylhydrazine to give phenylazoimide. But by quantitative examination it has now been found that excess nitrite, representing about 20 per cent. over and above that required to form the azoimide had to be added before an end-

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point was reached. It has been found that besides phenylazoimide being formed by the reaction

 $\mathrm{NHPh}\cdot\mathrm{NH}_2 + \mathrm{HNO}_2 \longrightarrow \mathrm{NO}\cdot\mathrm{NPh}\cdot\mathrm{NH}_2 + \mathrm{H}_2\mathrm{O} \longrightarrow \mathrm{PhN}_3 + 2\mathrm{H}_2\mathrm{O},$

a diazo-compound results simultaneously. By coupling with β-naphthol, benzeneazo-β-naphthol was obtained, being identified after crystallisation by its melting point. This secondary reaction, which may become the principal reaction under chosen conditions (Altschul, J. pr. Chem., 1896, [ii], 54, 496), is no doubt brought about by the oxidising action of the nitrous acid, and accounts for the excess nitrite required in the titration. This view is rendered the more probable in that Chattaway (T., 1908, 93, 852) has shown that aromatic hydrazines are converted into diazo-compounds by On the other hand, it has been shown that diazochlorine. compounds are also formed by the action of nitrous acid on nitrosocompounds (O. Fischer, Annalen, 1889, 255, 144; Hantzsch, Ber., 1902, 35, 894). The production of a diazo-compound by the interaction of phenylhydrazine and nitrous acid confirms the observation of Rügheimer (Ber., 1900, 33, 1718), who obtained benzenediazonium nitrate by passing nitrous oxide into a solution of nitrosophenylhydrazine in dry ether.

Owing to these complications, the use of nitrous acid was abandoned and the method adopted for the estimation of the phenylhydrazine was that described by Strache (*Monatsh.*, 1892, **13**, 299), which consists in collecting the nitrogen liberated on boiling with Fehling's solution. By this method, only free phenylhydrazine is estimated, but not any present as hydrazone. Distillation methods for estimating the ammonia were found satisfactory provided the production of tarry matters was avoided. The titration of the ammonia in the distillate was done with N/10hydrochloric acid with litmus as indicator, aniline salt reacting as free acid to this indicator.

Both phenylhydrazine and p-nitrophenylhydrazine have been employed in this work; the glucose used was anhydrous and was found by polarimetric estimation to be of 99.1 per cent. and by copper reduction of 99.2 per cent. purity.

The result of the analytical work is given in the table on page 225.

In each set of experiments the glucose and phenylhydrazine were dissolved in a mixture of 190 c.c. of water and 10 c.c. of glacial acetic acid. The solution was heated for two hours on a waterbath, when it was allowed to cool and the osazone filtered off, dried, and weighed. The filtrate was made up to a measured volume and aliquot parts were analysed.

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| | | Phenyl- glucosazone. | <i>p</i> -Nitrophenyl glucosazone. |
|--|---------|-------------------------|------------------------------------|
| Grams of glucose taken | | 3.60 | 1.80 |
| Grams of the hydrazine taken | ••• | 6·48 | 4.59 |
| Yield of osazone | ••• | 3.68 | 3.03 |
| Hydrazine used to form osazone (calculated | ed) | 3.33 | 3.09 |
| Free hydrazine found in solution | · | 2.13 | 1.05 |
| Hydrazine not accounted for | ••• | 1.02 | 0.45 |
| Glucose not accounted for | | 1.75 | 0.585 |
| Hydrazine required to convert the pr | eceding | | |
| quantity of glucose into hydrazone | | 1.05 | 0.497 |
| Ammonia found by distillation | | 0.182 | 0.120 |
| Ammonia calculated from vield of osazon | е | 0.174 | 0.112 |
| | | | |

Although these results do not represent that degree of accuracy which is usually demanded in quantitative determinations, they are as good as could be expected considering the difficulties which were encountered. They sufficiently indicate, however, that the equation generally used to represent the formation of the osazone of glucose is justified. It is further inferred from the analytical data that the glucose which is not converted into the osazone is present in the solution mainly as glucosephenylhydrazone.

The yields of osazone obtained in the two quantitative experiments described above (51 and 67 per cent., respectively, of those theoretically possible) not being considered satisfactory, it was decided to ascertain whether by the choice of more suitable conditions they could not be materially increased. To this end, glucose and phenylhydrazine were caused to interact in the proportions demanded by theory and under various conditions. The time chosen in these experiments was three hours, it having been ascertained that the yield of osazone was only very slightly increased by continuing the heating for longer periods. The temperature was the same in all cases, that is, that of the water-bath, for it was found that at lower temperatures the interaction was considerably retarded, whilst at higher temperatures tarry by-products were liable to be formed.

Before these experiments were undertaken it was thought that owing to the low yield of phenylglucosazone the reaction might be of a reversible character and the effect of the addition of aniline acetate and of ammonium acetate to the reacting mixture was ascertained; instead of diminishing the yield these additions were found to increase it. On the other hand, it was found on one occasion that doubling the amount of phenylhydrazine had the effect of increasing the yield of glucosazone by about 10 per cent.

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Effect of concentration on the yield.

The following quantities were employed : 3.6 grams of glucose, 6.48 grams of phenylhydrazine, and 10 c.c. of glacial acetic acid.

| C.c. of solution | 400 | 200 | 150 | 100 | 50 |
|--------------------|-----------|-----|-----|-----|----|
| % Yield of osazone | 29 | 45 | 66 | 78 | 82 |

Effect of acetic acid on the yield.

The quantities employed were the same as in the preceding table except in the case of the acetic acid, the amount of which was varied. The total volume was 100 c.c.

| C.c. of acetic acid | 2 | 6 | 10 | 14 | 20 | 30 |
|---------------------|----------|----|----|----|-----------|----|
| % Yield of osazone | 36 | 71 | 81 | 82 | 84 | 77 |

It should be noted that the diminution in the yield of osazone at high acetic acid concentration is not due to partial solubility in this acid, for the yield stated includes the slight amount obtained by diluting the acid. In the higher concentrations of acetic acid, the product was dark coloured owing to tarring.

The striking result obtained by varying the amount of acetic acid affords a possible explanation of the increased yield, alluded to above, which occurs on the addition of the acetates of aniline and ammonia to the system.

It is thus seen that although the interaction of glucose with phenylhydrazine to form phenylglucosazone did not in any case go to completion, it gave under suitable conditions yields which leave no doubt that it was the main reaction.

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