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ACTION OF ACID AMIDES UPON BENZOIN.¹

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THE reactions of benzoïn with a great number of bodies have been very extensively studied, but except the work of Anschütz and Gelderman² with urea and thiourea, no work has been done with the extensive class of acid amides. It was with the view of studying how these bodies would react with benzoïn that this work was undertaken. It seemed very probable that by heating the amides with benzoïn a condensation would be effected, as the hydrogen and the amido group of the former, as well as both the carbonyl and hydroxyl group of the latter, are very reactive. It was hoped in this way to prepare a series of condensation products from the amides of the homologous acids of the fatty and of the aromatic series. With this object in view, benzoïn was heated in sealed tubes with various acid amides, in the presence of alcohol as a solvent, in varying proportions and under different conditions of time and of temperature.

Instead of finding the expected series of condensation products, however, it was discovered that with all the simple amides of both the mono- and dibasic acids of the fatty series, and with

¹ From the author's thesis presented to the University of Pennsylvania for the Degree of Ph.D., 1895.

² *Ann. Chem.* (Liebig), 261, 129.

two examples of the amides of the aromatic series, the reaction was preceded by the breaking down of the amide and the subsequent action of the ammonia on the benzoin, giving as the chief product of the reaction tetraphenylazine $C_4N_2(C_6H_5)_4$. The constitution of this body has been very carefully worked out by Japp and Wilson¹ and Japp and Burton.²

Not until after the action of several of the series had been tried with benzoin was the above conclusion reached, hence the following is a record of the reactions tried and of the results obtained. The work was carried out to a great extent in sealed tubes, the yields obtained were in many cases very small, the separation of the bodies produced difficult, and in some cases impossible, while the analyses were frequently extremely troublesome, as tetraphenylazine is remarkably stable and, as the experience of others has also shown, very difficult to analyze. As an instance of this, in one analysis, after six hours heating to redness with oxide of copper in a current of oxygen, graphitic carbon was found still remaining in the bottom of the boat. Later chromate of lead was used and the difficulties in great measure overcome.

I. GENERAL METHOD PURSUED IN STUDYING THE REACTIONS.

As the reactions of benzoin, with ten different amides, were studied, and the identification of the products proved more difficult than was anticipated, no attempt was made to induce condensation by means of dehydrating agents. In all the experiments, unless otherwise stated, benzoin and the amide, in definite, but varying proportions, were heated together with alcohol in sealed tubes. The amount of alcohol used at first was considerable, but the loss from explosions was so great that eventually the tubes were filled to but one-fifth or sixth of their capacity. When the tubes were opened there was generally a very considerable pressure. The presence of ammonia was very evident, and in many cases an ethereal odor was easily detected. Even if no ammonical odor could be detected, the alkaline reaction of the tube contents was always decided. Analyses of the gases obtained from the tubes showed from twenty-five per cent.

¹ *J. Chem. Soc.*, 49, 825.

² *Ibid.*, 49, 843, and 51, 98.

to thirty-three per cent. of free ammonia. As the chief product of the reaction was identified as tetraphenylazine, and the accompanying bodies were those also produced by the action of ammonia on benzoïn, there can be no doubt as to the interpretation of the result. Under the influence of the heat and alcohol the amide breaks down with the liberation of ammonia, and the formation of an ester with the alcohol. The ammonia then reacts with the benzoïn, as has been already studied by Japp, Wilson and Burton.¹

Japp and Wilson, in their study of the action of ammonia on benzoïn, have reviewed the ground previously studied by Laurent² and by Erdmann³ and found the products of the reactions to be tetraphenylazine $C_4N_2(C_6H_5)_4$, benzoïniam $C_{28}H_{24}N_2O$, benzoïnidam $C_{28}H_{28}NO_2$, and lophine $C_8N_2H(C_6H_5)_3$. In the study of the products of reaction with the amides, the presence of tetraphenylazine was proved in all cases, the presence of lophine in but one, benzamide, while another body was obtained which proved to be a mixture of the benzoïniam and benzoïnidam of Japp and Wilson.

The tetraphenylazine was identified by analysis, melting point, crystalline form, solubilities, color reaction with sulphuric acid, and also by a determination of the molecular weight. In the work, as given in detail later, some or all of these means of identification were used in each case. Lophine was identified by its melting point. It was only obtained with benzamide as the reacting body, and then only in very small amount. The apparent reason for its occurrence in this case will be discussed under the work with benzamide.

The other body obtained had, under various conditions, different melting points, and did not give concordant results when the different preparations were analyzed. Various methods of fractional crystallization and sublimation were tried to separate it into bodies of definite composition, but without success. With the exception of its solubility in alcohol, all its reactions indicated, as already stated, a mixture of benzoïniam and benzoïnidam.

¹ *Loc. cit.*

² *Jsb. phys. Wiss.*, 18, 354, and 26, 266.

³ *Ann. Chem. (Liebig)*, 135, 181.

This action of the acid amides with benzoin, as essentially that of ammonia alone, is entirely in accord with the results obtained by Mason.¹ He found that oxamide and acetic acid heated together in sealed tubes at 220° – 230° , reacted with the formation of acetamide.

II. ACTION OF THE AMIDES OF THE FATTY SERIES UPON BENZOIN.

a. Malonamide and Benzoin.—Malonamide and benzoin, in molecular proportions, were heated with alcohol on the water-bath in a flask connected with a return condenser for an hour. An examination of the material showed that no change had taken place, only benzoin and malonamide being found. The two bodies, in the same proportion, were then heated with alcohol in a sealed tube to 110° in a paraffine bath. As no change took place the tube was then heated at temperatures varying from 130° to 190° , with but little apparent change. The tube was then heated for eighteen hours at 200° . When opened a considerable pressure was evident and the odor of ammonia was very decided. The contents of the tube were poured out, and the crystals which had separated were filtered from the deep yellow liquid, pressed between filter-paper and treated several times with warm chloroform. Everything dissolved except a small amount of unchanged malonamide. The filtered solution was then evaporated nearly to dryness, the residue warmed with alcohol to remove coloring-matter, boiled four times with alcohol, and the insoluble portion dissolved in chloroform. From the first alcoholic filtrate on cooling crystals were obtained, melting, not at all sharply, at 190° – 217° . The second filtrate gave white needles, melting at 192° – 206° ; the third filtrate crystals of the same form in less amount, melting at 193° – 206° . The other two alcoholic filtrates yielded thicker needles in small quantity, melting at 243° – 244° .

The three portions of crystals with the lower melting point were united and alternately treated with warm and boiling alcohol. By this means a series of products was obtained with all degrees of melting points between 193° and 220 . As the mate-

¹*J. Chem. Soc.*, 55, 107.

rial is all easily soluble in chloroform and in benzoïn, this gave no means of separation. An attempt at separation by means of sublimation was equally unsuccessful, the products showing the same wide range of melting point.

The three lots of crystals with high melting point and evidently much less soluble in alcohol than the other body, were united, warmed with alcohol, and the residue dissolved in chloroform. On concentration of the solution large transparent crystals were obtained with a melting point of 245° .

The above method of separation and purification has been given in detail, as it was used with all the amides. Many portions of benzoïn and malonamide were subjected to the above treatment, and the product with the melting point of 245° was proved to be tetraphenylazine by the results of the following examination :

Substance.	H ₂ O	CO ₂		
I. 0.1351	0.0611	0.4384		
II. 0.1416	0.0637	0.4585		
III. 0.1339	0.0568	0.4343	burned with copper oxide gave 13.8 cc. nitrogen at 26° and 764 mm.	
IV. 0.2004 gram				
Calculated for Tetraphenylazine.				
C ₂₈ H ₂₀ N ₂	I.	II.	Found. III.	IV.
Carbon 87.50	88.49	88.30	88.45
Hydrogen 5.21	5.02	4.99	4.71
Nitrogen 7.29	7.68

The melting point of tetraphenylazine as given by Japp and Wilson is 246° ; the melting point as obtained for the body under consideration is 245° (uncorrected).

The molecular weight determination was made by the Raoult method, using benzene as the solvent. A Beckmann thermometer, graduated to 0.01° , was used, with the well-known Beckman apparatus. The results were as follows :

$$\begin{aligned}
 L &= 21.8262 \\
 C &= 0.162 \\
 P_{100} &= 27.38 \\
 \text{Hence } CL &= 3.5358 \\
 A &= 0.1291 \\
 M &= 379.5 \\
 \text{Calculated for } C_{28}H_{20}N_2 &= 384
 \end{aligned}$$

With concentrated sulphuric acid this body gives a beautiful red color, a very characteristic reaction for tetraphenylazine.

An analysis of the gas from one of the tubes in which the benzoin and malonamide had been heated, showed twenty-nine per cent. of ammonia.

b. Oxamide and Benzoin.—Oxamide and benzoin were heated together in molecular proportions at about 200°. The reaction at times took place with violent explosions and appeared to require a temperature of 200°, as below this repeated attempts failed to produce any change. The bodies obtained were separated by the method already described. They were identical with those yielded by malonamide. One of them melted at 244°, gave a red color with concentrated sulphuric acid, and crystallized from chloroform in prisms of the usual form. A molecular weight determination was as follows :

$$\begin{aligned} L &= 20.5973 \\ C &= 0.201 \\ P\ 100 &= 29.19 \\ \text{Hence } CL &= 4.1400 \\ A &= .1418 \\ M &= 345.6 \\ C_4N_2(C_6H_5)_4 &= 384 \end{aligned}$$

The other body gave an indefinite melting point from 193°-217°. Repeated crystallization failed to produce any body with a definite melting point.

I. 0.1073 gram burned with copper oxide gave 5.1 cc. nitrogen at 23° and 766.5 mm. = 5.39 per cent. nitrogen.

II. 0.1005 gram gave 4.9 cc. nitrogen at 25° and 763 mm. = 5.44 per cent. nitrogen.

Analyses of samples of gas from the tubes showed from twenty-five to thirty-three per cent. of free ammonia.

c. Succinamide and Benzoin.—Benzoin and succinamide were heated in molecular proportions at 200° for thirty-five hours. When the contents of the tube were treated in the usual way no unchanged succinamide remained, showing a complete decomposition. From the chloroform solution the same body separated in the usual crystalline form, melting at 245° and giving a deep red color with sulphuric acid. A molecular weight determination gave the following results :

$$\begin{aligned}
 L &= 17.9414 \\
 C &= 0.175 \\
 P_{100} &= 27.73 \\
 \text{Hence } CL &= 3.1397 \\
 A &= 0.1381 \\
 M &= 354 + \\
 C_4N_2(C_6H_5)_4 &= 384
 \end{aligned}$$

From the alcoholic filtrates white crystals were obtained melting from 192° – 207° , with in one instance a small portion not melting until 216° . The analysis gave the following.

0.1033 gram burned with copper oxide gave 5.9 cc. nitrogen at 26.5° and 761 mm. = 6.32 per cent nitrogen.

It will be noticed that this analysis shows a considerable difference from that of the similar body obtained from oxamide. This is another reason for supposing this body to be a mixture of benzoinam and benzoinidam. The former has the formula $C_{28}H_{24}N_2O$, giving 6.93 per cent. nitrogen and melting at "temperatures varying from 190° – 220° , according as the temperature was raised slowly or rapidly." The latter has the formula $C_{28}H_{22}NO$, giving 3.45 per cent. nitrogen, and melting at 199° . That a mixture of these two bodies would give the results obtained as mentioned above, is natural. In the work of Japp and Wilson sufficient alcohol was put in the tubes to hold in solution much of the material produced, and hence the two bodies were separated. In the reactions, as carried out with the acid amides, the pressure of the evolved gases was so great that but little alcohol could be used. Hence only a small amount of the material produced was held in solution by the alcohol. This fully accounts for the non-separation of the two bodies by the method described by Japp and Wilson.

In order to compare the bodies obtained by the action of the amides upon benzoïn with those obtained by the method as described by Japp and Wilson, benzoïn was heated in sealed tubes with alcoholic ammonia. One tube was heated at 150° – 180° for eight hours. The contents were then examined in the usual way and by means of the melting point tetraphenylazine was found to have been formed, together with a body melting finally at 210° , but softening much below this. A second tube,

heated at 200° for several hours, also showed the formation of tetraphenylazine, but only very slight traces of any body melting at about 200° . But what was doubtless lophine was found in considerable amount, as shown by the isolation of a body melting at 272° . These reactions indicate that at higher temperatures lophine is produced, while at lower temperatures benzoinam is obtained in larger amount. This conclusion is strengthened by the observation that with only one amide was any lophine detected. This was with benzamide, which did not react with benzoin, except at temperatures much above those used with the other amides. It is true that the temperature at which the other amides react without producing lophine was equal to or even above that at which lophine was formed by the direct action of alcoholic ammonia. But this could be caused by the greater heat required for the breaking down of the amides. It seems quite possible that this might offer a means of studying the constitution of benzoinam.

d. Acetamide and Benzoin.—Benzoin and acetamide, in molecular proportions, heated together at 150° for four hours, did not react. Further heating at 190° – 210° for six hours was also without effect. In a second tube the amount of acetamide was doubled and the tube heated for six hours at 150° , without any reaction taking place. In the next experiment four times the molecular quantity of acetamide was used for the benzoin employed, making about two grams of each and the tube was heated at 190° – 210° for nearly six hours. When opened the odor of ethyl acetate was very evident, and an examination of the material showed that a reaction had taken place. Another tube with four grams of each was then heated at 190° – 200° for six hours. When opened the odor proved both ethyl acetate and ammonia to be present. By means of repeated boilings with alcohol the usual bodies were separated and identified.

The tetraphenylazine melted at 242° , gave a deep red color with concentrated sulphuric acid, and crystallized from chloroform in the usual prismatic crystals. From the earlier alcoholic extracts bodies were obtained, melting at 192° – 194° and 206° – 209° . The yields were very small; but these observations would indicate that the reaction had taken place in the same manner as shown before.

e. Butyramide and Benzoïn.—Butyramide was prepared by the method of Hofmann.¹

In the first experiment 0.8 gram of the butyramide was heated with one gram of benzoïn at 200° for six hours. No action took place. The tube was then heated for six hours at 250°; when opened the odor of ammonia was strong, and an ethereal odor was readily detected. A second tube, with double the above quantities of material, was then heated for eight hours at 200°, and for four hours at 220°. The contents of the two tubes were united and worked up as before with the usual results. The tetraphenylazine melted at 246°, gave an intense red color with sulphuric acid, and crystallized from chloroform in the usual prismatic form. The body soluble in alcohol melted at 193°–205°. In this instance the tetraphenylazine did not appear to be the principal product of reaction, as it was produced in much less amount than the lower melting body. This differs very decidedly from the usual reaction. The yields were small.

f. Valeramide and Benzoïn.—In the first experiment with benzoïn and valeramide one gram of each was used and the tube heated four hours at 200°. As no action had taken place it was then heated for several hours at temperatures varying from 230°–280°. When opened the usual combination of ammoniacal and ethereal odors was observed. Examinations of the small amount of product showed that a reaction had taken place.

To obtain more of the substance two more tubes, with larger amounts of material, were heated for several hours at from 220°–270°, until a change was evident. The contents of the three tubes were then worked up as before with the usual results. The yield obtained was very small, but tetraphenylazine was identified by the melting point of 246°, the red color with sulphuric acid and the crystalline form. The other body melted at 193°–209°. As with butyramide, the relative proportion of the products was different from that observed with the amides of the dibasic acids, tetraphenylazine being produced in smaller amount than the other body.

III. ACTION OF THE AMIDES OF THE AROMATIC SERIES UPON BENZOïn.

a. Benzamide and Benzoïn.—Molecular proportions of benzoïn

¹ *Ber. d. chem. Ges.*, 15, 981.

and benzamide were first heated together in an oil-bath at 120° . No action took place. The tube was then heated at 150° – 160° . Examination of the tube contents showed unchanged benzoin and benzamide and nothing else. A second tube, with the same amount of material (two grams of benzoin), was heated for six hours at 190° – 200° , but without producing any reaction. Another tube, with double the amount of benzamide heated at 190° – 200° for several hours, gave the same results, unchanged benzoin and benzamide being found, without anything else.

As these experiments had shown that benzamide would not react with benzoin under the same conditions that the other amides did, further trials were made at higher temperatures, with better results. The first tube prepared with the amount of alcohol which had usually been used were all lost by explosion, at temperatures between 220° and 250° . The next tube prepared contained only a very small amount of alcohol with benzoin and benzamide in the molecular proportions of 1 to 2. It was first heated four hours at 250° without producing any change. A second heating for seven hours at 250° – 260° was also without apparent action. Then for seven hours the tube was heated at 290° – 300° , a portion of the time the temperature even rising to 360° . When the tube was opened there was no pressure apparent, the odor of ammonia was but slight, but the alkaline reaction of the liquid was strong. The yield of crystals obtained was very small, but melting point determinations showed that a change had taken place, with indications of the production of tetraphenylazine and of some body with a higher melting point.

Another tube, prepared in the same way, was heated for seven hours at 250° – 265° . As the crystals were deposited on cooling, the tube was opened and the contents examined. The yield was very small, but separation in the usual way, by means of boiling alcohol and chloroform, showed the formation of at least two bodies, which from their melting points indicated lophine and tetraphenylazine. There was no indication whatever of the presence of the bodies with melting points of about 200° and which were found as a part of the products of reaction of all the other amides with benzoin. As the only different condition

here was that of higher temperature, the same conclusion is reached that was pointed to with the experiments with alcoholic ammonia and benzoïn, *i. e.*, the higher the temperature of reaction the less the amount of benzoïn-am and the greater the amount of lophine which is formed.

b. Salicylamide and Benzoïn.—When heated together in the proportion of two molecules of salicylamide to one of benzoïn, for six hours at 200° , the reaction was easily induced. When the tube was opened a slight pressure was evident, the liquid had a faintly alkaline reaction, but no odor of ammonia, while that of a salicylic ester was very noticeable. An examination of the crystals obtained from the tube was made in the usual way by means of treatment with boiling alcohol and chloroform.

Tetraphenylazine was found and identified by its melting point, color reaction with sulphuric acid and crystalline form. From the alcoholic extracts the usual body separated, with melting points varying from 192° – 207° . Salicylamide therefore reacted just as the fatty amide did. About one-fifth of the original amide used was found unchanged in the liquid drained from the crystals in the tube.

In order to determine whether the amides would react with benzoïn directly, without the intervention of a solvent, experiments were tried by heating them together in a dry condition.

When malonamide and benzoïn were mixed together and heated by means of a paraffine bath at about 160° , action commenced and there was an evolution of gas, which proved to be ammonia. At 170° , the melting point of malonamide, the effervescence was very rapid. The heating was continued until the reaction had about ceased, and, on cooling, the reddish crystalline mass was boiled with alcohol and the residue dissolved in chloroform. The melting point determinations showed that tetraphenylazine had been produced, with slight traces of benzoïn-am.

Succinamide, when heated with benzoïn in the same way, was also found to react with the evolution of ammonia. Benzamide, even when heated to 200° with benzoïn, under the same conditions, was without action. These results are entirely in accord with those obtained in the presence of alcohol, and under pressure.

IV. THEORETICAL DEDUCTIONS.

Although in the nature of a repetition, the results of this work with amides may be summed up as follows :

Acid amides, heated with benzoin in alcoholic solution, do not yield condensation products in the true sense of the term, but break down with the liberation of ammonia and the formation of an ester with the alcohol. The ammonia then reacts with the benzoin in the way already studied by others.¹ This reaction takes place with the greatest ease with malonamide, and only with great difficulty and at high temperatures with benzamide. In every case tetraphenylazine is a constant product, while benzoinam and benzoinidam are produced at lower temperatures, lophine at higher. The presence of alcohol is not necessary to induce the breaking down of the amide, as the same results are obtained by the simple interaction of the dry materials. The great difference between the reactions of benzamide and of salicylamide is of interest as another example of the weakening of the benzene ring by the presence of hydroxyl in the nucleus of the latter.

V. A STUDY OF TETRAPHENYLAZINE.

a. Historical.—As tetraphenylazine was found to be the chief product of the action of amides upon benzoin, a further study of this body was instituted.

A brief review of what has been done in its preparation and investigation may be of interest. Laurent studied² the action of ammonia on benzoin. Later Erdmann³ took up the same study and gave the name benzoinimide to what has since been shown to be tetraphenylazine by Japp, Wilson⁴ and Burton. The very interesting work of these later investigators showed, that on distillation with lime, the so-called benzoinimide of Erdmann was converted into diphenanthyleneazotide, as it was then called. Ammonia acting on β -naphthoquinone was shown to produce $\alpha\beta$ -naphthazine, a body whose constitution had been already proved through its syntheses by Witt⁵ by the condensa-

¹ *Loc. cit.*

² *Ann. Chem.* (Liebig), 66, 181, and *Jsb. phys. Wiss.*, 18, 354, and 26, 666.

³ *Ann. Chem.* (Liebig), 135, 181.

⁴ *J. Chem. Soc.*, 49, 825 and 843, and 51, 98.

⁵ *Ber. d. chem. Ges.*, 19, 2794.

tion of β -naphthoquinone with $\alpha\beta$ -diamidonaphthalene. As ammonia acting on phenanthraquinone yields the "diphenanthyleneazotide" this was also considered an azine, tetraphenyleneazine, and hence the so-called ditolaneazotide, which by distillation with lime yields the tetraphenyleneazine, was itself given the proper name tetraphenylazine.

Braun and Meyer¹ have produced this same body by the action of sodium amalgam on benziloxime, and have called it tetraphenylaldine. The only substitution product of tetraphenylazine which has been obtained is the tetra-nitro derivative prepared by Braun and Meyer. Attempts were, therefore, made to obtain bromine and chlorine derivatives, but, as the results will show, without success.

To obtain the material for study, the tetraphenylazine was prepared by the method described by Japp and Wilson, by heating benzoïn with ammonium acetate in an open flask, and separating the azine from the other products of the reaction by means of alcoholic hydrochloric acid. This was found to be an entirely satisfactory method and gave a good yield of pure material, melting at 245° .

b. Bromination.—The azine was first heated with carbon bisulphide and an excess of bromine for eleven hours on the water-bath with return condenser. Acid vapors were given off in slight amount. An examination of the material showed that no bromination had taken place, the azine being found unchanged, melting at 245° . A second experiment was made by boiling a solution of the azine in strong alcoholic hydrochloric acid with bromine. An examination of the material showed that the azine was unaffected.

In the third experiment, chloroform was used as the solvent and bromine was added in the calculated quantity to produce a tetra-brom substitution product. Acid vapors were given off and the separation of dark red crystals appeared to indicate that a substitution had taken place. These, on exposure to air, rapidly lost their color, and by treatment with alcohol yielded the unchanged azine, as shown by the melting point and the absence of any halogen. Some of the reactions, as the action

¹ *Ber. d. chem. Ges.*, 21, 1269.

toward solvents, seemed to indicate that an unstable addition product might have been formed, but it is more probable that the red crystals represented simply a mechanical mixture of bromine with the azine. A repetition of the above, with the addition of a few crystals of iodine, gave the same results.

In the next trial some of the azine was heated in a sealed tube with bromine, a crystal of iodine and alcohol for seven hours at 200° – 220° . When the contents were examined it was found that ethyl bromide and acetic acid had been formed, but that the azine was not brominated. The ethyl bromide was identified by its boiling point (38° – 40°) and odor, and the acetic acid by its boiling point (115° – 123°), and the formation of acetic ether with alcohol and sulphuric acid. The dark residue, when extracted with chloroform, gave the unchanged azine, melting at 244° . The insoluble black residue appeared to be carbon, not melting at 300° , insoluble in acids, alkalies or the usual solvents, burning with glowing, and not containing any halogen.

c. Chlorination.—Tetraphenylazine was dissolved in chloroform, and through the solution contained in a retort placed on the water-bath and connected with a return condenser, a stream of dry chlorine gas was passed for six hours. An examination of the material showed that no change had taken place. The same material was then subjected to the action of chlorine again, for the same length of time, with the same result. Aluminum chloride was then added to the contents of the retort and a rapid stream of chlorine was passed through for six hours, for a part of this time the retort being in direct sunlight. The residue, after removal of the solvent, was boiled with water, well washed, dried, and dissolved in chloroform. An examination of the material showed that no halogen had entered the body. Hence neither bromine nor chlorine substitution products could be obtained by the action of the halogens on tetraphenylazine. This great stability of the phenyl groups in the azine ring is of interest, and entirely in accord with analogy.

d. Nitration and Amidation.—Following the method employed by Braun and Meyer¹, the tetranitro derivative of tetraphenylazine was prepared by slowly adding the azine to cold, fuming

¹ *Loc. cit.*

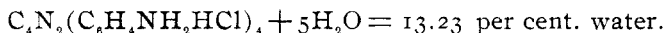
nitric acid, with stirring. The deep yellow liquid was then poured into an excess of cold water, and the resulting voluminous light yellow powder filtered out, washed, and dried. It has an indefinite melting point between 140° and 150° . With concentrated sulphuric acid it gives an orange yellow color, very different from the brilliant red yielded by the unchanged azine.

To prepare the amido derivatives, the tetranitroazine was reduced with tin and hydrochloric acid. The clear red solution was diluted with water and the tin removed with hydrogen sulphide. The removal of the last portions of tin was extremely difficult, as not until repeated treatment with the hydrogen sulphide in a nearly neutral boiling solution could a base be obtained free from ash. When the filtrate from the sulphide of tin was made alkaline with ammonia an abundant yellow precipitate was obtained. During the filtration a portion of this appeared to undergo oxidation, as the precipitate, at first yellow, became green on the surface, and the filtrate, at first clear, became turbid on standing. The well-washed precipitate finally ceased to give a turbid filtrate and dissolved in hydrochloric acid with red color. Hydrogen sulphide, when passed into this solution, gave no precipitate. The solution was boiled, to remove the hydrogen sulphide, and made alkaline with ammonia, when a yellow precipitate was thrown down, which when filtered and washed, showed no change of color and gave a clear filtrate. When dried this base is of a brownish yellow color, is slightly soluble in chloroform, more readily in boiling alcohol. From the latter solution, on evaporation, it is obtained as before, in an amorphous condition without any sign of crystallization. When heated it darkens and melts above 260° , with decomposition and a slight sublimation.

To determine its composition, the hydrochloride was prepared by dissolving some of the base in dilute hydrochloric acid and evaporating the solution over sulphuric acid in a vacuum desiccator. No crystals could be obtained, but the material dried to a reddish-brown, transparent mass. It melts at about 140° , and is readily soluble in water. When the material, which had been dried over sulphuric acid, was heated to 100° in the air-bath, its

loss in weight would indicate five molecules of water of crystallization.

0.2867 gram, after heating at 100° , weighed 0.2480 gram = 13.49 per cent. water.



0.2480 gram hydrochloride, dried at 100° , gave 0.2243 gram AgCl.

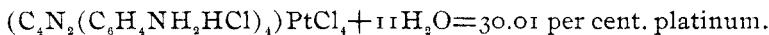
Calculated for
 $\text{C}_4\text{N}_2(\text{C}_6\text{H}_4\text{NH}_2\text{HCl})_4$.
 24.06 per cent. chlorine.

Found.
 22.33 per cent. chlorine.

Platinic chloride, added to the aqueous solution of the hydrochloride, precipitates on standing a reddish-brown double salt.

0.1090 gram platinum double salt gave 0.0325 gram platinum = 29.81 per cent. platinum.

This corresponds to a salt of the composition :



The filtrate mentioned before as obtained from the precipitation of the base by ammonia becomes turbid on standing and slowly precipitates a dark greenish-blue material. When acidified with hydrochloric acid it gives a dark green solution, which, under certain conditions of dilution, gives a deep blue color. This, when treated with hydrogen sulphide or zinc and hydrochloric acid, changes to green and finally to a yellow color. Standing exposed to the air, it gradually reverts to the blue color, while heating with nitric acid quickly produces the same change.

All these reactions indicate the presence of another base, possibly of two others of different composition. Their constitution was not further investigated.

e. Crystallographic and Optical Investigation.—As tetraphenylazine crystallizes from chloroform in brilliant prismatic crystals, an examination of the crystallographic and optical constants was made with the following results :

SYSTEM TRICLINIC.

$$\tilde{a} : \tilde{b} : c = 0.941^{\circ} : 1 : 0.5611.$$

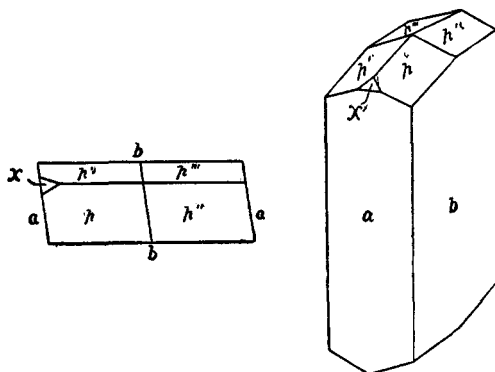
$$\alpha = 83^{\circ} 48' \quad \beta = 85^{\circ} 13' \quad \gamma = 101^{\circ} 38'.$$

$$100 \wedge 010 = 101^{\circ} 13' \quad 1^{\circ}\text{P} \wedge 010 = 72^{\circ} 36'.$$

$$\text{Calculated } 001 \wedge 010 = 86^{\circ} 20' \quad 001 \wedge 100 = 84^{\circ} 36'.$$

FORMS.

a (100 i-i)	p (III P')	p ₂ (III ₁ P)
b (010 i-i)	p ₁ (II' P)	p ₃ (III P')
x (405 $\frac{1}{3}$ -i)		



OBSERVED ANGLES.

ab = 101° 13'	b ₁ p ₁ = 80° 4'	p ₂ p ₃ = 26° 35'
bp = 72° 36'	ap = 68° 47'	p ₁ p ₃ = 35° 33'
bp ₁ = 79° 23'	ap ₁ = 73° 12'	p ₁ p ₂ = 26° 30'
b ₁ p ₃ = 73° 16'	pp ₂ = 35° 2'	ax = 55° 42'

Crystals flat, tabular parallel to 010.

Cleavage none.

Optically negative, as determined by a quarter undulation mica plate.

Plane of optic axes parallel to c.

Apparant axial angle $2E = 18^\circ$.

EXTINCTION ANGLES.

On b.....parallel to edge ab.

On a.....parallel to edge ab.

On section normal to c = 14° with b.

Indices of refraction determined by the microscope method, using sodium light.

On b with edge ab normal to principal section of Nicol	= 1.873
" " " " parallel " "	= 2.217
On a " " " normal " "	= 1.946
" " " " parallel " "	= 1.897

VI. ACTION OF BENZOIN UPON UREA AND THIOUREA.

While studying the action of amides with benzoïn, the reac-

tions with urea and thiourea were examined. Not until after considerable work had been done was it found that Anschütz and Gelderman¹ had previously studied these reactions and published their conclusions. The results that were obtained fully corroborated those of these chemists, and so will not be given in detail.

a. Urea and Benzoïn.—Urea and benzoïn, when heated together with alcohol in sealed tubes at 175°–195°, do not react as the true amides do, but form condensation products, with the elimination of water. That they react in this manner is to be accounted for by the fact that the two amido groups are both linked to the same carbon atom. It would be interesting to see whether the amides of the amido acids of the fatty and aromatic series would undergo condensations of the same nature.

The body obtained by the condensation of urea and benzoïn dissolves in boiling alcohol, with a beautiful blue fluorescence, and crystallizes in prismatic forms, which are dichroic. In the earlier work on these substances, it was found that under certain conditions this body is dimorphous, coming out from solution in two entirely distinct forms, one prismatic, as just mentioned, and the other in bunches of very delicate white needles. When the two forms were very carefully mechanically separated and dissolved in boiling alcohol, each solution, on cooling, showed crystals of both forms. The tendency was toward the assumption of the prismatic form. All attempts at ascertaining the conditions under which these could be produced were fruitless. Later work failed to give the needle form, only the prisms being obtained. That the two bodies were identical was shown by the melting points and a determination of the nitrogen content. Both softened at about 280° and melted, not sharply, at about 318°. Analyses gave the following results :

NEEDLE FORM.

0.1023 gram substance, burned with copper oxide, gave 11.4 cc. nitrogen at 23° and 763 mm. = 12.59 per cent. nitrogen.

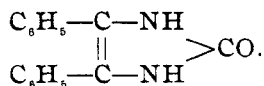
PRISMATIC FORM.

0.2022 gram gave 23.5 cc. nitrogen at 23° and 759.5 mm. = 12.70 per cent. nitrogen.

¹ *Loc. cit.*

The two bodies are therefore identical.

Extended study by Anschütz, Gelderman, and Schwickerath¹ has shown this body to be diphenylacetylenurein.



Analysis of the prismatic crystals mentioned above confirm this.

0.2203 gram substance gave 0.1044 gram water, and 0.6123 gram carbon dioxide.

	Calculated for $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}$.	Found.
Carbon	76.27	75.77
Hydrogen	5.09	5.26
Nitrogen	11.86	12.70
Oxygen	6.78	

Evans² has shown that condensations of urea with β -diketones can be induced by the influence of acids on their alcohol solution. Similar experiments were therefore tried with urea and benzoïn. Urea was added to a saturated alcoholic solution of benzoïn, and different amounts of concentrated hydrochloric acid added. No condensation was, however, produced.

b. Thiourea and Benzoïn.—The thiourea used was prepared from ammonium thiocyanate. When heated with benzoïn a condensation takes place, with the formation of what Anschütz and Schwickerath have shown to be $\alpha\beta$ -diphenylglyoxaline sulphydrate. In the experiments with this body the two forms of crystals, as mentioned under the urea derivative, were produced, but the prismatic form was in very much the greater quantity, the needle form being only observed in very small amount. An attempt at producing the needle form in larger amount was made by using, instead of thiourea alone, a mixture of equal parts of this and ammonium thiocyanate. The results, however, were the same, only traces of the needle form appearing. This confirms the work of Anschütz, who found that the same body was produced whether thiourea or ammonium thiocyanate was used.

¹ *Loc. cit.*, and *Ann. Chem. (Liebig)*, 284, 8.

² *J. prakt. Chem.*, 48, 489.