XCIX.—*Syntheses of Piazine Derivatives. Interaction of Benzylamine and Phenacyl Bromide.**

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Theoretical Summary.

DURING the last decade, the interaction of phenacyl bromide and amines has several times been made the subject of detailed experimental investigation. E. Braun and Victor Meyer have shown that with ammonia the primary product is *eso*amidoacetophenone (*Ber.*, **21**, 1269).

This compound is a strong base, and very stable in acid solution. If set free by soda, 2 mols. condense, 1 mol. H_2O being eliminated, together with 2 atoms of hydrogen, the product $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}$ being formed; this in presence of ammonia loses another mol. H_2O with formation of 2:5-diphenylpiazine. In order to explain these metamorphoses, it is simplest to assume that, under the observed con-

* From Dr. Winder's "Dissertation." Zürich, 1893.

ditions, esoamidoacetophenone acts in the desmotropic or pseudo-form, $\text{C}_6\text{H}_5\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{NH}_2$ (von Baeyer, *Ber.*, **16**, 2189; P. Jacobson, *Ber.*, **21**, 2228, footnote; Michael, *J. pr. Chem.*, **42**, 19, **45**, 581, and **46**, 207; Rathke, *Ber.*, **18**, 3110, and **20**, 1057; Bamberger, *Ber.*, **23**, 1868). The formation of these compounds may then be explained by the following equation.

Aniline reacts easily with phenacyl bromide, as Möhlau found (*Ber* **14**, 172 and **15**, 2467), forming phenacylanilide.

and the tendency to the formation of an anilide is so great that when dimethylaniline and phenacyl bromide are brought together, a methyl group is eliminated, and phenacylmethylanilide formed.

By warming with zinc chloride, the anilides form indole derivatives by simple condensation with elimination of 1 mol. H_2O (Staedel, *Ber.*, **21**, 2197).

Indole derivatives are also obtained on heating the anilides with aromatic amines, but in this case the reaction is more complicated, the compounds formed not being identical with those obtained by the aid of zinc chloride. The reaction can, however, be explained by assuming the formation of intermediate products (Staedel, *loc. cit.*, and Bischler, *Ber.*, **25**, 2860).

The amine first combined with the phenacyl group is thus eliminated in the final reaction. In a subsequent paper, it will be shown by one of us that a second phenacyl group can be introduced into the phenacylanilide molecule, and that the diphenacylaniline thus obtained reacts easily with amines, 2 mols. H_2O being eliminated, and closed rings formed.

We find now that the interaction of phenacyl bromide and benzylamine is more complicated than either of the cases cited above, namely, with ammonia or aniline, for even when 2 mols. of benzylamine are used for 1 mol. of the bromide, both monophenacyl- and diphenacyl-benzylamine are formed.

These compounds were isolated in the form of hydrobromides, and numerous experiments showed that on setting the bases free with alkali, a change takes place, and that the oils obtained can be but very partially reconverted into salts.

Two molecules of the first base condense, with elimination of 2 mols. H_2O , and 1 : 4-dibenzyl- 2 : 5-diphenylpiazine dihydride is formed, the condensation being analogous to that of esoamidoacetophenone.

On heating 1 : 4-dibenzyl- 2 : 5-diphenylpiazine dihydride to boiling, toluene is given off, and from the residue 2 : 5-diphenylpiazine can be isolated, the compound being identical with that from esoamidoacetophenone, $\text{N}\begin{smallmatrix} \text{CH}\cdot\text{C}(\text{C}_6\text{H}_5) \\ \text{C}(\text{C}_6\text{H}_5)\cdot\text{CH} \end{smallmatrix}\text{N}$.

The second base, diphenacylbenzylamine, on being set free, is in all probability converted, with the loss of 1 mol. H_2O , into the oxazine $\text{O}\begin{smallmatrix} \text{C}(\text{C}_6\text{H}_5)\cdot\text{CH} \\ \text{C}(\text{C}_6\text{H}_5)\cdot\text{CH} \end{smallmatrix}\text{N}\cdot\text{C}_7\text{H}_7$ (Ber., 22, 2081 and 2094).

On standing with cold alcoholic ammonia, the hydrobromide of diphenacylbenzylamine is converted quantitatively into an amide, $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_5):\text{CH}$, $\text{NH}_2\cdot\text{C}(\text{C}_6\text{H}_5):\text{CH}$ $\text{N}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$, which at 100° loses 1 mol. H_2O , 2:6-diphenyl-4-benzylpiazine dihydride being formed.

The same condensation takes place on warming the amide with dilute hydrochloric acid, the hydrochloride of the hydro-base being formed.

The hydride, as also its hydrochloride, on continued heating, yields 2:6-diphenylpiazine, with elimination of toluene and benzylic chloride respectively:—

By the action of aniline on diphenacylbenzylamine hydrobromide, the synthesis of 1:2:6-triphenyl-4-benzylpiazine dihydride was effected,

but owing to the difficulty experienced in preparing it in quantity, no further experiments were made with it.

Benzylamine reacts easily at 120° with diphenacylbenzylamine hydrobromide, 1:4-dibenzyl-2:6-diphenylpiazine dihydride being formed in approximately theoretical quantity,

and the more minute examination of its behaviour towards reagents revealed some very interesting molecular transpositions. On heating with concentrated hydrochloric acid in sealed tubes, two atoms of hydrogen are eliminated; the compound formed is devoid of basic

properties, and is not acted on by benzoyl chloride or acetic anhydride, and, therefore, probably has the constitution

On heating 1:4-dibenzyl-2:6-diphenylpiazine dihydride alone to 260—270°, toluene is eliminated, the remaining benzyl group “wandering” from nitrogen to carbon, and 2:6-diphenyl-3-benzylpiazine being formed.

Lastly, on treatment with alcoholic ferric chloride and hydrochloric acid, the dihydride parts with one benzyl group as benzyl chloride, and the hydrochloride of the same diazine hydride is formed which was obtained directly from amidodiphenacylbenzylamine by warming it with dilute hydrochloric acid, namely, 2:6-diphenyl-4-benzylpiazine dihydride, $\text{HN} \begin{array}{c} \langle \text{C}(\text{C}_6\text{H}_5):\text{CH} \\ \text{C}(\text{C}_6\text{H}_5):\text{CH} \rangle \text{N}\cdot\text{C}_7\text{H}_7.$

In the above general view of the action of benzylamine on phenacyl bromide, almost exclusive use has been made of the desmotropic or pseudo-formula, with hydroxyl radicles, and we are of the opinion that this formula gives a very plausible explanation of the reactions observed. We do not assert that the hydroxyl formula represents the true constitution of these compounds when in a state of chemical inactivity, and it is quite possible that reactions may be discovered which necessitate the use of the ketone formula. We hoped to obtain valuable evidence in this direction by the preparation of oximes and hydrazones, but our efforts have hitherto been fruitless.

It is almost superfluous to state that the whole research forms another weighty argument for the existence of the “para-bond” in true diazines.

Preparation of Mono- and Di-phenacylbenzylamine.

The reaction is best conducted in alcoholic solution, an excess of amine being avoided, otherwise, as it is a stronger base than either of the products formed, it will combine with the hydrogen bromide formed during the reaction, at the expense of the other two compounds; in this way a mixture of the bases will be formed which can only be incompletely converted into the corresponding salts.

53 grams (1 mol.) of benzylamine and 100 grams (1 mol.) of phenacyl bromide are separately dissolved in alcohol, and the solu-

tions mixed, the total quantity of alcohol used being about 400 c.c. The solution gradually becomes hot and dark, acquires a reddish-brown colour, and, on standing over night, the diphenacylbenzylamine hydrobromide separates almost completely in small, white needles. The salt is collected with the aid of the water pump, washed well with alcohol, and then with lukewarm water, until a few drops of the filtrate leave no residue on evaporation; the salt, which has become slightly yellow, is then washed again with alcohol until white, and dried on porous plates. In some of the experiments made, the crude product seemed to be quite free from monophenacylbenzylamine hydrobromide, whereas in others a very appreciable quantity was removed by the warm water, the salt separating again from the filtrate in long needles. The brown filtrate from the diphenacylamine salt is evaporated on the water bath to a small bulk, and allowed to cool, all the mono-salt and the greater part of the benzylamine hydrobromide separating in the crystalline form. The mass is crushed in a mortar, collected by the aid of the pump, and washed with benzene and light petroleum until the filtrate is colourless. After drying on a porous plate, it is redissolved in as small a quantity of boiling water as possible, when a small amount of diphenacylbenzylamine salt remains undissolved, and can be filtered off hot, and washed with a little hot water. The hot filtered solution deposits the mono-salt, on standing, in the form of long, white needles, which are collected and washed with a small quantity of cold water. On working up the mother liquors, another small amount of the mono-salt can be recovered, and by evaporating the filtrate to dryness and extracting with benzene until the residue is nearly white, the greater part of the benzylamine hydrobromide can be recovered. Working by this method, the yield of the respective salts was as follows.

Diphenacylbenzylamine hydrobromide	51 grams.
Monophenacylbenzylamine hydrobromide..	25 ,,
Benzylamine hydrobromide.....	24 ,,

Monophenacylbenzylamine Salts.

The *hydrobromide*, $C_{15}H_{15}NO, HBr$, obtained as above, crystallises from water and alcohol in long, white needles. The melting point of the salt, from water, is $202-203^{\circ}$, and of that from alcohol, $201-202^{\circ}$. For analysis, it was dried over sulphuric acid.

0.1628 gave 0.350 CO_2 and 0.0856 H_2O . $C = 58.63$; $H = 5.84$.

0.2180 ,, 0.1343 $AgBr$. $Br = 26.21$.

0.2358 ,, 9.5 c.c. moist nitrogen at 20° and 721 mm. $N = 4.39$.

$C_{15}H_{15}NOBr$ requires $C = 58.82$; $H = 5.23$; $N = 4.57$; $Br = 26.14$ p.c.

It is only sparingly soluble in cold water, but easily in hot, and also in hot alcohol. On boiling it with dilute nitric acid, and allowing the clear solution to stand, benzoic acid melting at 119° separates.

Hydrochloride, $C_{15}H_{15}NO, HCl$.—Concentrated hydrochloric acid is evaporated repeatedly on the water bath with the pure hydrobromide until the needles are converted into small, white plates; after the product has been recrystallised twice from alcohol, from which it also separates in plates, it melts at 215° . A chlorine determination, in a sample dried over sulphuric acid, was made.

0.2183 gave 0.1203 AgCl. $Cl = 13.60$.

$C_{15}H_{15}NOCl$ requires $Cl = 13.54$ per cent.

It is sparingly soluble in cold water or alcohol, easily in hot water, and very easily in hot alcohol.

Platinochloride, $(C_{15}H_{15}NO)_2, H_2PtCl_6$.—The hydrochloride is dissolved in as small a quantity of hot water as possible, a few drops of concentrated hydrochloric acid added, and then excess of hot aqueous platinic chloride. The salt separates immediately in small, orange crystals. The air dried salt was analysed.

0.1612 gave 0.0363 Pt. $Pt = 22.52$.

0.1512 „ 0.0341 Pt. $Pt = 22.55$.

0.1070 „ 0.0241 Pt. $Pt = 22.52$.

0.1541 „ 0.1546 AgCl. $Cl = 24.11$.

$(C_{15}H_{15}NO)_2, H_2PtCl_6$ requires $Pt = 22.69$; $Cl = 24.71$ per cent.

The salt does not lose weight when heated at 110° , but at 120° gradual decomposition takes place. It is moderately soluble in hot water and hot alcohol.

Sulphate, $C_{15}H_{15}NO, H_2SO_4$.—The hydrobromide was gradually added to about twice its weight of concentrated sulphuric acid in a porcelain basin, stirring well all the time; streams of hydrogen bromide were evolved, and the mixture assumed a reddish colour. It was then heated on the water bath until a drop of the liquid dissolved in water gave no precipitate with silver nitrate; the brown liquid thus obtained was diluted with water and filtered. On standing, the salt was deposited in glistening, prismatic needles which became colourless on recrystallisation. It was dried over sulphuric acid for analysis.

0.1270 gave 0.0965 $BaSO_4$. $S = 10.43$.

0.1290 „ 0.0930 $BaSO_4$. $S = 9.90$.

$C_{15}H_{15}NO, H_2SO_4$ requires $S = 9.91$ per cent.

The salt is moderately soluble in cold water, and insoluble in alcohol.

Picrate, $C_{15}H_{15}NO, C_6H_2(NO_2)_3.OH$.—Solutions of the hydrobromide and picric acid in boiling alcohol were mixed and heated for 10 minutes on the water bath and allowed to cool; the long, glistening, yellow needles which separated were recrystallised from alcohol, when they melted at $151-152^\circ$. For analysis, the compound was dried over sulphuric acid.

0.1767 gave 20 c.c. moist nitrogen at 16° and 714 mm. $N = 12.38$.

0.1963 „ 22 c.c. „ „ „ 14.7° and 712 mm. $N = 12.29$.

$C_{15}H_{15}NO, C_6H_2(NO_2)_3.OH$ requires $N = 12.33$ per cent.

The compound is easily soluble in hot alcohol, but only sparingly in benzene and toluene, and insoluble in ether or light petroleum.

Monophenacylbenzylamine.

If the pure hydrobromide is mixed with alcohol, and soda solution added, the salt dissolves with a yellow coloration on shaking; and on the addition of water, an oil is precipitated, which is for the greater part soluble in hydrochloric acid. It was washed with water, taken up with ether, the ethereal solution dried with solid soda, and the ether distilled off, when a thick, transparent, reddish-brown oil remained; this, however, even on long standing, did not show any signs of crystallisation. It had a characteristic sweet and penetrating smell, and was easily soluble in alcohol, ether, and benzene. It was found, however, that it was only very sparingly soluble in boiling, dilute hydrochloric acid, a semi-solid mass remaining which contained 1 : 4-dibenzyl-2 : 5-diphenylpiazine dihydride (see below). The fact that the freshly precipitated base is far more easily soluble in acid shows that monophenacylbenzylamine is very unstable, 2 mols. condensing with formation of an indifferent product.

1 : 4-Dibenzyl-2 : 5-diphenylpiazine Dihydride,

Monophenacylbenzylamine hydrobromide was heated on the water bath with concentrated soda solution for three quarters of an hour; the reddish-brown oil thus formed, after being washed with hot water, became very thick on cooling. It was dissolved in hot alcohol, and the solution allowed to stand over night, when bright yellow needles separated in small quantity; these melted at 163° after recrystallisation from the same solvent. The compound was dried at 100° and analysed.

0.1392 gave 0.4424 CO_2 and 0.0774 H_2O . $C = 86.67$; $H = 6.10$.

0.1022 „ 6 c.c. moist nitrogen at 13° and 720 mm. $N = 6.57$.

$C_{30}H_{26}N_2$ requires $C = 86.95$; $H = 6.28$; $N = 6.76$ per cent.

A determination of the molecular weight by Raoult's method gave the following results.

	I.	II.
Weight of substance taken..	0.1821 grams.	0.4729 grams.
Weight of phenol	15.36 „	15.36 „
Observed depression	0.217°	0.581°
Molecular weight found	415	402
Theory for $C_{30}H_{26}N_2$	414	

The compound is easily soluble in ether, benzene, and toluene in the cold, moderately in hot alcohol, but only sparingly so in cold alcohol or light petroleum. It is not affected by concentrated hydrochloric acid, but dissolves in cold concentrated sulphuric acid, giving a yellow solution, which turns brown on warming; on adding water, the original compound is precipitated, but much darker in colour. The yield is a bad one, only 3 grams being obtained from 25 grams of the hydrobromide. We thought that this might be due in some measure to an inner condensation with formation of an isoquinoline derivative, but our efforts to isolate such a product were futile.

3 grams of 1:4-dibenzyl-2:5-diphenylpiazine dihydride were carefully heated over a naked flame in a small test tube, the open end of which had been drawn out and bent, so as to form a very small retort. Shortly after the melting point had been reached, a lively ebullition set in, the colour changed from intense yellow to light brown, and a small quantity of a yellow liquid distilled over. The distillate was rectified, and gave 0.14 gram of a colourless, mobile, highly refractive liquid distilling at 110°, and possessing the characteristic smell of toluene.

The light brown residue, on cooling, solidified to a crystalline mass, which, after washing with alcohol, was recrystallised from the same solvent. 0.6 gram of small, pinkish plates were thus obtained, the melting point being 192—193°. For analysis the substance was dried at 100°.

0.1265 gave 0.3833 CO_2 and 0.0612 H_2O . C = 82.63; H = 5.37.

0.2135 „ 23 c.c. moist nitrogen at 19.5° and 718 mm. N = 11.62.

$C_{16}H_{12}N_2$ requires C = 82.76; H = 5.17; N = 12.06 per cent.

The compound is only sparingly soluble in the ordinary solvents. The melting point we found 1° lower than that given by Braun and Meyer (*Ber.*, 21, 1279), and in order to establish the identity of the product the following experiments were made.

On heating in a small glass tube, a yellow, crystalline sublimate was formed. The compound was insoluble in dilute hydrochloric acid, soluble in the concentrated acid on heating, and reprecipitated by water; the solution in concentrated acid deposited fine yellow needles on standing. Sulphuric acid also dissolved the compound with a reddish-yellow colour, and water precipitated it again unaltered. These are all characteristic reactions for the 2 : 5-diphenylpiazine obtained by Braun and Meyer (*loc. cit.*) directly, by the condensation of 2 mols. of esoamidoacetophenone in presence of ammonia.

so that there cannot be the least doubt as to the identity of the compound.

Diphenacylbenzylamine Salts.

The *hydrobromide*, $\text{C}_{23}\text{H}_{21}\text{NO}_2\cdot\text{HBr}$, was recrystallised from boiling alcohol, in which it is sparingly soluble; it forms small, white needles melting at $196-197^\circ$. For analysis, it was dried over sulphuric acid.

0.1076 gave 0.2570 CO_2 and 0.0511 H_2O . $\text{C} = 65.14$; $\text{H} = 5.27$.

0.2087 „ 0.0924 AgBr . $\text{Br} = 18.84$.

0.1194 „ 3.5 c.c. moist nitrogen at 18.5° and 721 mm. $\text{N} = 3.20$.

$\text{C}_{23}\text{H}_{21}\text{NO}_2\cdot\text{HBr}$ requires $\text{C} = 65.09$; $\text{H} = 5.19$; $\text{N} = 3.30$; $\text{Br} = 18.86$ per cent.

The salt is decomposed by continued boiling with water.

Hydrochloride, $\text{C}_{23}\text{H}_{21}\text{NO}_2\cdot\text{HCl}$.—Concentrated hydrochloric acid was evaporated repeatedly on the water bath with the pure hydrobromide. The product was washed well with cold water, and recrystallised twice from hot alcohol, from which it separated in white needles melting at $189-190^\circ$. The salt was dried over sulphuric acid and analysed.

0.1556 gave 0.0611 silver chloride. $\text{Cl} = 9.63$.

$\text{C}_{23}\text{H}_{21}\text{NO}_2\cdot\text{HCl}$ requires $\text{Cl} = 9.33$ per cent.

It is partially soluble in hot water with decomposition, and easily in hot alcohol.

Platinochloride, $(\text{C}_{23}\text{H}_{21}\text{NO}_2)_2\cdot\text{H}_2\text{PtCl}_6$.—To a hot alcoholic solution of the hydrochloride acidified with concentrated hydrochloric acid, excess of alcoholic platonic chloride was added, and the solution allowed to stand. The double salt separated in large, shining, yellow plates. The air dried salt was analysed.

0.2902 gave 0.0515 Pt . $\text{Pt} = 17.74$.

$(\text{C}_{23}\text{H}_{21}\text{NO}_2)_2\cdot\text{H}_2\text{PtCl}_6$ requires $\text{Pt} = 17.80$ per cent.

It is insoluble in alcohol, water, and aqueous hydrochloric acid, but moderately easily soluble in alcoholic hydrochloric acid.

Diphenacylbenzylamine.

The behaviour of the base is very similar to that of monophenacylbenzylamine. On setting it free with soda, it forms a light brown, thick oil, soluble in hydrochloric acid; after extracting with ether, however, drying the ethereal solution, and removing the ether by distillation, a thick, red, transparent oil is obtained, which is not soluble in hydrochloric acid, and which, in all probability, contains the oxazine $O < \begin{smallmatrix} C(C_6H_5):CH \\ C(C_6H_5):CH \end{smallmatrix} > N \cdot C_7H_7$.

It is easily soluble in alcohol, ether, and benzene.

Action of Ammonia on Diphenacylbenzylamine Hydrobromide. Amido-diphenacylbenzylamine, $\begin{smallmatrix} OH \cdot C(C_6H_5):CH \\ NH_2 \cdot C(C_6H_5):CH \end{smallmatrix} > N \cdot C_7H_7$.

Ten grams of the hydrobromide were added quickly to a 15 per cent. solution of alcoholic ammonia, which had been previously cooled in ice-cold water, and well shaken until the salt had entirely dissolved. After standing a short time, the amido-compound began to separate from the yellow solution in pale-yellow, well-formed tables, and in 12 hours the separation was complete. The product was collected by the aid of the pump, and washed with cold alcohol; it cannot be recrystallised without considerable loss, but, as the analyses show, the product is pure. The yield is almost quantitative. The melting point is not sharp; it darkens at 65°, begins to sinter at 70°, and is completely melted at 80°. The substance was dried over sulphuric acid and analysed.

0.1217 gave 0.3613 CO₂ and 0.0702 H₂O. C = 80.96; H = 6.40.

0.1656 „ 0.4903 „ 0.0985 „ C = 80.74; H = 6.60.

0.1491 „ 11.3 c.c. moist nitrogen at 18° and 720 mm. N = 8.28.

C₂₃H₂₂N₂O requires C = 80.70; H = 6.43; N = 8.18 per cent.

The compound is moderately soluble in cold alcohol, easily in hot, and also in cold ether, benzene, and toluene, but insoluble in water.

On standing several weeks in a desiccator, or closed tube, the substance darkens very much, and becomes semi-fluid, owing to inner condensation, with elimination of water, 4-benzyl-2:6-diphenyl-piazine dihydride being formed (see below).

Platinochloride, (C₂₃H₂₂N₂O)₂.H₂PtCl₆ + 3H₂O.—On dissolving the amide in alcohol, a yellow solution is obtained, which, on the addition of concentrated hydrochloric acid, turns dark-red. Alcoholic platinic

chloride gives no precipitate in this solution, but if water be afterwards added, a deep violet platinum salt separates. The amide also dissolves in dilute hydrochloric acid, with a dark-red colour, and aqueous platinic chloride precipitates from such a solution the same salt as above. It was collected, washed with water, and dried on a porous plate; after standing 24 hours, it formed a dark-violet, amorphous powder.

0.1211 gave 0.0102 H₂O at 110°, and on ignition 0.0202 Pt. H₂O = 8.42; Pt = 16.68.

0.1109 gave 0.0202 Pt. Pt = 18.21.

(C₂₃H₂₂N₂O)₂.H₂PtCl₆ + 3H₂O requires H₂O (5 mols.) = 7.84. Pt = 17.00 per cent. (C₂₃H₂₀N₂)₂.H₂PtCl₆ requires Pt = 18.44 per cent.

The salt, on drying at 110°, changes from violet to yellow, and the numbers given above show that not only the water of crystallisation is eliminated at that temperature, but that the inner condensation to the piazine derivative also takes place, the yellow salt being the platinochloride of 4-benzyl-2:6-diphenylpiazine dihydride (see below), and the violet one the platinochloride of the amide. This condensation seems to take place slowly at ordinary temperatures, the violet salt gradually becoming lighter in colour on the surface.

4-Benzyl-2:6-diphenylpiazine Dihydride, $\text{NH} \begin{smallmatrix} \text{C}(\text{C}_6\text{H}_5):\text{CH} \\ \text{C}(\text{C}_6\text{H}_5):\text{CH} \end{smallmatrix} \text{N} \cdot \text{C}_7\text{H}_7$.

The amide described above was heated in a test tube partly immersed in a paraffin bath; when the temperature of the latter had risen to about 90°, the compound melted to a dark-red, opaque liquid, small glass bubbles rose to the surface, and water began to condense in the upper part of the tube; the water was removed with a coil of filter paper. At 120—130°, the liquid became transparent, and from that temperature up to 140—150°, also lighter in colour; when no more water condensed in the tube, the reaction was complete. On cooling, the product formed a transparent, semi-solid mass of a light red colour. It is not advisable to heat higher than 150°, as toluene then begins to distil and 2:6-diphenylpiazine is formed (see below). The dihydride is insoluble in water, sparingly soluble in light petroleum (35—55°), moderately in hot alcohol, and easily in ether or benzene. As the compound could not be obtained in a form suitable for analysis, the action of acetic and benzoic anhydride was studied, but in both cases dark-coloured, semi-solid masses were obtained, from which nothing crystalline could be isolated. By the action of benzylic chloride on the hydride, we hoped that it would be

possible to prepare 1:4-dibenzyl-2:6-diphenylpiazine dihydride, $C_7H_7 \cdot N < \begin{smallmatrix} C(C_6H_5):CH \\ C(C_6H_5):CH \end{smallmatrix} > N \cdot C_7H_7$, which we afterwards obtained directly from diphenacylbenzylamine and benzylamine, but in place of that compound we obtained a mixture of two very stable substances, 5-benzyl-2:6-diphenylpiazine and 3:5-dibenzyl-2:6-diphenylpiazine, which also came under our notice at a subsequent stage of the research, and which are formed by a highly interesting molecular transposition of the product we hoped to obtain, in which the benzyl radicles "wander" from nitrogen to carbon. Both compounds are fully described later on, so that it is unnecessary to enter into detail here.

Hydrochloride, $C_{23}H_{20}N_2 \cdot HCl + 3H_2O$.—The semi-solid dihydride dissolves in dilute hydrochloric acid forming a deep-red solution, which, on warming for some time on the water bath, loses most of its colour, becoming pale-yellow; on cooling, the hydrochloride separates out in pale-yellow needles. After one recrystallisation from water containing a little free acid, they are quite pure, and melt at 193° to a pale yellow liquid. After standing several days over soda, the salt was analysed.

0.1800 gave 0.0612 AgCl. Cl = 8.39.

0.2029 „ 0.0272 H_2O on drying at 110° . H_2O = 13.45.

$C_{23}H_{20}N_2 \cdot HCl + 3H_2O$ requires Cl = 8.54; H_2O = 13.03 per cent.

The salt is easily soluble in cold alcohol and hot dilute hydrochloric acid.

Platinochloride, $(C_{23}H_{20}N_2)_2 \cdot H_2PtCl_6$.—The hydrochloride was dissolved in hot water containing free hydrochloric acid, and excess of aqueous platinic chloride added. The double salt separated immediately as a bright orange, crystalline powder. The salt was dried over sulphuric acid and analysed.

0.3267 lost 0.0017 on drying at 110° , and gave on ignition 0.0597 Pt. Pt = 18.36.

$(C_{23}H_{20}N_2)_2 \cdot H_2PtCl_6$ requires Pt = 18.44 per cent.

The above loss of 0.0017 gram water is equivalent to 0.5 per cent.; theory for 1 mol. H_2O = 1.6 per cent. In the calculation of the platinum the loss at 110° was subtracted from the amount of salt taken.

During the platinum estimation, a liquid condensed on the lid of the crucible; on cooling, it solidified, and gave the melting point $85-87^\circ$, that of 2:6-diphenylpiazine.

This base may be prepared either directly from 4-benzyl-2:6-diphenylpiazine dihydride or from the hydrochloride.

Preparation from the Dihydride.—The thick, red oil obtained by heating amidodiphenacylbenzylamine to 150° was heated in a test tube over a small, free flame. A lively ebullition soon set in, and the liquid became much paler in colour; the toluene given off condensed in the upper part of the tube, and was removed by a roll of filter paper. After cooling, a little alcohol was added, the mixture warmed until everything was dissolved, then cooled again, and the sides of the tube vigorously rubbed with a glass rod until crystals began to separate; or, if the compound was already to hand, it was found better merely to add a few crystals and allow the mixture to stand. The crude product thus obtained when recrystallised from a small quantity of alcohol, formed small, white needles. In this method of preparation, it is important that the heating be quickly performed, otherwise the piazine only separates in small quantity from the alcoholic solution, and on long standing; in normal experiments, however, the yield was satisfactory.

Preparation from the Hydrochloride.—The salt was heated in a test tube immersed in a bath of Wood's metal; at $190\text{--}200^\circ$, the hydrochloride melted to a yellow liquid, and the characteristic smell of benzylic chloride was noticed. The bath was gradually heated to 210° , and kept at that temperature for about 15 minutes, the benzylic chloride being taken up with filter paper. The product was a reddish-brown oil, which, on cooling, solidified to an almost white, crystalline mass; it was washed with a little alcohol, and then recrystallised from the same solvent.

Both preparations melted at $88\text{--}89^\circ$, and, after drying over sulphuric acid, were analysed.

I. From the dihydride.

0.1385 gave 0.4207 CO_2 and 0.0657 H_2O . C = 82.84; H = 5.24.

0.1011 „ 11.2 c.c. moist nitrogen at 15° and 717 mm. N = 12.22.

II. From the hydrochloride.

0.1326 gave 0.4009 CO_2 and 0.0652 H_2O . C = 82.45; H = 5.46.

0.1309 „ 14.5 c.c. moist nitrogen at 18° and 720 mm. N = 12.11.

$\text{C}_{16}\text{H}_{12}\text{N}_2$ requires C = 82.76; H = 5.17; N = 12.06 per cent.

The base is insoluble in water, moderately soluble in cold alcohol and light petroleum, and very easily in ether, benzene, and toluene. If comparatively large quantities of the compound are allowed to

crystallise slowly from dilute alcohol, glistening, white needles can be obtained, over an inch in length. When heated to boiling with dilute hydrochloric acid, the piazine simply melts, but, on adding concentrated acid and heating again, the oil solidifies, with formation of the hydrochloride. The base dissolves in cold sulphuric acid with an orange-yellow colour, which becomes deeper on warming; the addition of water gives a white precipitate of the unaltered substance.

The molecular weight of the base was determined by Raoult's method in phenol, the following numbers being obtained.

	I.	II.
Weight of substance taken....	0.3040 grams	0.7703 grams.
Weight of phenol.....	19.27 „	19.27 „
Observed depression	0.54°	1.37°
Molecular weight found	222	222
Theory for $C_{16}H_{12}N_2$	232	

All three of the diphenylpiazines indicated by theory are now known. The 2:3-compound was prepared by one of us by the action of ethylenediamine on benzil (Trans., 1889, 55, 99), and 2:5-diphenylpiazine was prepared from esoamidoacetophenone directly, as also from monophenacylbenzylamine, by methods described at the beginning of this paper.

Platinochloride, $(C_{16}H_{12}N_2)_2, H_2PtCl_6$.—The base was dissolved in a small quantity of alcohol, concentrated hydrochloric acid added, and the hot solution mixed with excess of alcoholic platinic chloride. The double salt separated quickly in golden-yellow scales, which were collected and washed with alcohol and ether. The salt was dried at 100° for analysis.

0.1876 gave on ignition 0.0416 Pt. $Pt = 22.17$.

$(C_{16}H_{12}N_2)_2, H_2PtCl_6$ requires $Pt = 22.25$ per cent.

It is insoluble in water and hydrochloric acid, and only sparingly soluble in alcohol.

Action of Benzylamine on Diphenylacylbenzylamine Hydrobromide.

1:4-Dibenzyl-2:6-diphenylpiazine Dihydride,

A mixture of 36 grams of diphenacylbenzylamine hydrobromide (1 mol.) and 18 grams of benzylamine (2 mols.) was heated in a flask immersed in a paraffin bath. The salt turned yellow in contact with the amine, and, on heating, the colour deepened to orange-red. The temperature was raised to 120—130°, water condensing in the upper

part of the flask and the salt gradually dissolving to an orange-red solution; the heating was continued until the formation of bubbles in the liquid and the evolution of water had ceased. On cooling, the product formed a semi-solid, orange-yellow mass; this was digested with cold ether, the solution filtered from the undissolved benzylamine hydrobromide formed during the reaction, and the greater part of the ether removed by distillation. The concentrated ethereal solution thus obtained was mixed with two or three times its volume of alcohol, and allowed to stand. The intensely yellow, crystalline mass which separated was recrystallised from alcohol, when small, bright yellow, semi-transparent cubes were obtained, melting at 86° . For analysis, the substance was dried over sulphuric acid.

0.1637 gave 0.5233 CO_2 and 0.0934 H_2O . $\text{C} = 87.18$; $\text{H} = 6.33$.

0.1767 „ 11 c.c. moist nitrogen at 19° and 719 mm. $\text{N} = 6.67$.

$\text{C}_{30}\text{H}_{26}\text{N}_2$ requires $\text{C} = 86.95$; $\text{H} = 6.28$; $\text{N} = 6.76$ per cent.

The compound is very easily soluble in cold ether, benzene, and toluene, moderately so in hot alcohol, sparingly in the cold, sparingly in light petroleum, and insoluble in water. With hot concentrated hydrochloric acid, it gives a beautiful, crimson coloration, intensified by the presence of alcohol; this changes, however, to the original intense yellow colour, on the addition of water. The compound dissolves in warm sulphuric acid with a yellow coloration, and, on adding water, a brownish-red precipitate is formed.

Platinochloride, $(\text{C}_{30}\text{H}_{26}\text{N}_2)_2, \text{H}_2\text{PtCl}_6 + 5\text{H}_2\text{O}$.—This base was dissolved in hot alcohol with the addition of hydrochloric acid, the deep red solution cooled, and aqueous platinic chloride added; the amorphous, reddish-brown precipitate was collected on a filter, washed with water, and dried on a porous plate. When dry, the product formed a rich, carmine powder. The air-dried salt was analysed.

0.1930 gave 0.0281 Pt. $\text{Pt} = 14.55$.

0.2000 „ 0.0294 Pt. $\text{Pt} = 14.70$.

$(\text{C}_{30}\text{H}_{26}\text{N}_2)_2, \text{H}_2\text{PtCl}_6 + 5\text{H}_2\text{O}$ requires $\text{Pt} = 14.68$ per cent.

The water of crystallisation could not be estimated; on heating in the benzene bath, the salt became paler in colour, and gave up water very gradually, but no constant weight was attained, even on heating for several days. At higher temperatures, the salt undergoes decomposition.

The compound dissolves sparingly in hot alcohol with a yellow colour, more easily in presence of free hydrochloric acid, giving a red solution. On boiling with water, the salt melts, but does not dissolve.

Molecular Transpositions of 1:4-Dibenzyl-2:6-diphenylpiazine Dihydride. Action of Hydrochloric acid. 3:5-Dibenzyl-2:6-diphenylpiazine, N $\begin{smallmatrix} \diagup C(C_6H_5):C(C_7H_7) \\ \diagdown C(C_6H_5):C(C_7H_7) \end{smallmatrix}$ *N.*

The above dihydride, when heated under pressure with concentrated hydrochloric acid, behaves in quite a different manner from its isomer 1:4-dibenzyl-2:5-diphenylpiazine dihydride, for whereas the latter, as already shown, easily gives up both benzyl groups in the form of toluene, and yields 2:5-diphenylpiazine, the former undergoes a molecular change, the benzyl groups being retained in the molecule, and only 2 atoms of hydrogen being eliminated. This behaviour recalls that of the formation of toluidine and xylydine by heating the hydrochlorides of monomethyl- and dimethyl-aniline at 300°.

$C_6H_5 \cdot N(CH_3)_2$ gives $CH_3 \cdot C_6H_4 \cdot NH \cdot CH_3$ and $C_6H_5(CH_3)_2 \cdot NH_2$.

On opening the tubes, after heating for several hours at 170°, a colourless gas escaped which burnt with a yellowish flame; the product formed was a transparent, brown, sticky mass, which became crystalline on stirring well with alcohol. It was collected on a filter, and recrystallised from boiling alcohol, from which it separated in small, almost colourless plates. The mother liquors turned dark olive-green on standing, but nothing further could be isolated from them. For analysis, the preparation was dried at 100°.

0.1333 gave 0.4269 CO_2 and 0.0726 H_2O . C = 87.34; H = 6.05.

0.1650 „ 0.5282 „ 0.0862 „ C = 87.30; H = 5.80.

0.1361 „ 8.8 c.c. moist nitrogen at 20° and 727 mm. N = 7.07.

$C_{30}H_{24}N_2$ requires C = 87.37; H = 5.82; N = 6.80 per cent.

The melting point of the compound was 146–147°. It is insoluble in water and light petroleum, only sparingly soluble in boiling alcohol, but easily in cold ether, benzene, and toluene. It dissolves in sulphuric acid with a yellow coloration which becomes darker on warming; water precipitates the substance unaltered. As the analyses show, the compound contains 2 atoms of hydrogen less than the parent substance, and, on examining the formulæ, it is easily seen that the only probable explanation is to be found in a “wandering” of the two benzyl groups from nitrogen to carbon, and the closing of the para-bond between the nitrogen atoms. In accordance with this view, the compound is not attacked by acetic anhydride or benzoic chloride. A molecular weight determination by Raoult's method in phenol gave the following numbers.

	I.	II.
Weight of substance taken	0.2565 grams	0.831 grams
Weight of phenol	14.56 „	14.56 „
Observed depression	0.340°	1.160°
Molecular weight found	393	374
Theory for $C_{30}H_{24}N_2$	412

On heating 1 : 4-dibenzyl-2 : 6-diphenylpiazine dihydride at 260—270°, one of the benzyl groups is eliminated as toluene, and the remaining one very probably changes its position from nitrogen to a neighbouring carbon atom.

Numerous experiments were made, using various quantities of dihydride, but the yield was most erratic even when apparently exactly the same conditions were observed. We will describe two of the trials which gave the best results.

Four grams of dihydride were heated in a test tube over a small free flame, and when all had melted, a thermometer was introduced. The temperature rose rapidly to 260—270°, and remained constant for a short time, a brisk evolution of toluene taking place. A gradual rise of temperature then set in, the liquid becoming very pale, and on continued heating until the thermometer registered 330°, a change of colour was observed, the product becoming light brown. The flame was then withdrawn, and on cooling and stirring well with a glass rod, the mass solidified, and had a strong odour of mushroom. The product was stirred with alcohol, collected, and recrystallised from the same solvent. The yield was 1.4 grams.

Five grams of dihydride were heated for 10 minutes at 260—270°, the product allowed to cool, and then stirred well with alcohol. The yield was 3 grams (theory 3.53). In a subsequent experiment, made in apparently exactly the same way, only 0.6 gram was isolated.

After recrystallising several times from alcohol, the compound formed a white, crystalline powder melting at 95°. The sample used for analysis was dried over sulphuric acid.

0.1013 gave 0.3186 CO_2 and 0.0530 H_2O . C = 85.77; H = 5.81.

0.1018 „ 0.3209 „ 0.0530 „ C = 85.97; H = 5.78.

0.1232 „ 9.5 c.c. moist nitrogen at 17° and 726 mm. N = 8.55.

$C_{23}H_{18}N_2$ requires C = 85.71; H = 5.58; N = 8.69 per cent.

The compound is insoluble in water and light petroleum, easily soluble in hot alcohol, only sparingly in the cold, but very easily in cold ether, benzene, or toluene. It is very sparingly soluble in con-

concentrated hydrochloric acid, and is reprecipitated by water. Concentrated hydrochloric acid does not decompose it at 170°, even after 10 hours' heating, and it is not affected by acetic or benzoic anhydride. The boiling point of the compound lies above 400°.

It dissolves in cold sulphuric acid with a yellow coloration, which remains on heating; the addition of water gives a white precipitate of the unaltered substance. The molecular weight determination gave the following numbers.

	I.	II.
Weight of substance taken....	0.2144 grams	0.6181 grams
Weight of phenol.....	14.53 „	14.53 „
Observed depression	0.370°	1.110° „
Molecular weight found	303	291
Theory for C ₂₃ H ₁₈ N ₂	322	

The stability of the compound when heated with hydrochloric acid at 170°, the analyses, the molecular weight, and the indifference towards acetic and benzoic anhydrides is all evidence in favour of the above formula.

Action of Ferric Chloride on 1 : 4-Dibenzyl-2 : 6-diphenylpiazine Dihydride in presence of Hydrochloric acid. Hydrochloride of 4-Benzyl-2 : 6-diphenylpiazine Dihydride,

Five grams of the dihydride were dissolved in about 50 c.c. of alcohol and 10 c.c. of concentrated hydrochloric acid; to the deep red solution, 5 grams of sublimed ferric chloride dissolved in 20 c.c. of alcohol were added, and the mixture boiled for half an hour on the water bath. On evaporating to dryness, a strong smell of benzylic chloride was noticed, the residue forming a black, crystalline mass; this was taken up with about 50 c.c. of alcohol and a few drops of hydrochloric acid, and mixed in a flask with 1 litre of hot water. Steam was then passed in until the smell of benzylic chloride had disappeared, and after standing a few minutes, the solution was decanted on to a plaited filter in a hot-water funnel. The residue was heated with more water, and the solution filtered into the first portion. The filtrate had a reddish colour, and deposited the hydrochloride in brown needles on standing. This was purified by dissolving it in water, when a small quantity of a brown, amorphous powder remained behind, filtering, and allowing to stand. Long, pale yellow needles were thus obtained, identical in every respect with the salt prepared directly from 4-benzyl-2 : 6-diphenylpiazine dihydride in the manner already described. The yield was 4.5 grams.

For analysis, it was recrystallised once more from water acidified with hydrochloric acid, when it melted at 193° . On drying to constant weight in a toluene bath, the crystals became dull yellow.

0.1452 gave 0.0576 AgCl. Cl = 9.75.

$C_{21}H_{20}N_2 \cdot HCl$ requires Cl = 9.82 per cent.

As a further proof of its identity, the salt was converted by heating into 2 : 6-diphenylpiazine, the melting point observed being $88-89^{\circ}$.

The formation of the above hydrochloride by the action of ferric chloride on 1 : 4-dibenzyl-2 : 6-diphenylpiazine dihydride is further evidence that 4-benzyl-2 : 6-diphenylpiazine dihydride really does contain an imide (NH) group, and as a necessary consequence that the product of the action of ammonia on diphenacylbenzylamine is really an amide, $\begin{matrix} OH \cdot C(C_6H_5) : CH \\ NH_2 \cdot C(C_6H_5) : CH \end{matrix} > N \cdot CH_2 \cdot C_6H_5$.

Action of Aniline on Diphenacylbenzylamine Hydrobromide. 4-Benzyl-1 : 2 : 6-triphenylpiazine Dihydride, $C_6H_5 \cdot N < \begin{matrix} C(C_6H_5) : CH \\ C(C_6H_5) : CH \end{matrix} > N \cdot C_7H_7$.

The hydrobromide was heated with aniline in a paraffin bath at 180° , in the proportions of 1 mol. of salt to 2 of the amine; water was given off, and, on cooling, the product formed a dirty-brown, crystalline mass. This was reduced to powder, extracted with cold and hot water, and filtered; the filtrate left aniline hydrobromide on evaporation, and smelled strongly of phenylcarbylamine. The insoluble residue was difficult to purify, repeated crystallisation from benzene, and afterwards from alcohol, being necessary before the melting point became constant. It was ultimately obtained in the form of yellowish-white plates melting at $184-185^{\circ}$. The substance was dried over sulphuric acid and analysed.

0.1260 gave 0.4010 CO_2 and 0.0646 H_2O . C = 86.80; H = 5.69.

0.1378 „ 9 c.c. moist nitrogen at 21° and 724 mm. N = 7.07.

$C_{29}H_{24}N_2$ requires C = 87.00; H = 6.00; N = 7.00 per cent.

The compound is insoluble in water, easily soluble in hot alcohol and light petroleum, and very easily in cold ether, benzene, and toluene. It dissolves in concentrated hydrochloric acid with a yellow coloration, and from this solution aqueous platinic chloride precipitates a dirty-brown platinochloride. It is soluble in sulphuric acid with a bright yellow coloration, the addition of water precipitating the original substance unaltered. The yield obtained was very small, owing to the difficulties met with in purification, and in consequence

the reactions carried out with 1:4-dibenzyl-2:6-diphenylpiazine dihydride were not followed in this case.

The subjoined diagrammatic scheme represents the transformations of diphenacylbenzylamine described in this paper.

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