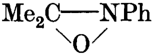
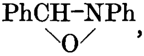
CCXI.—*The Constitution of the Condensation Product of β-Phenylhydroxylamine and Acetone.*

By FRANCIS HARROLD BANFIELD and JOSEPH KENYON.

A CONCENTRATED solution of β-phenylhydroxylamine in acetone deposits, after about two weeks, large, rhombic crystals which melt at 136°. To this compound Bamberger and Rudolf, who first described it (*Ber.*, 1907, **40**, 2237), gave the constitution  $\underset{\diagdown O \diagup}{\mathrm{Me_2C{-\!-}NPh}}$ by analogy with  $\underset{\diagdown O \diagup}{\mathrm{PhCH{-}NPh}}$,* at that time regarded as the constitution of the condensation product of β-phenylhydroxylamine and benzaldehyde. Beckmann and Scheiber (*Annalen*, 1907, **355**, 235) showed, by molecular-weight determinations, that the empirical formula must be doubled, and prepared analogous

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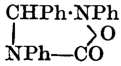
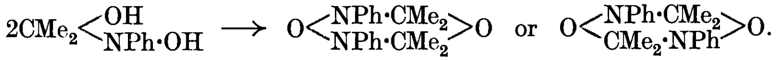
* Bamberger subsequently (*Ber.*, 1922, **55**, 3376; 1924, **57**, 2082) replaced this formula by PhCH:NPh:O in accordance with the modern formulation of azoxy-compounds, and support for the new constitution is afforded by the formation of the additive compound  $\begin{array}{l}\mathrm{CHPh{\cdot}NPh}\\ | \qquad\quad >\mathrm{O}\\ \mathrm{NPh{-\!-}CO}\end{array}$ with phenylcarbimide.

compounds from acetone and β- *p*- and *m*- (but not *o*-) tolyl- and β-(α-naphthyl)-hydroxylamines. They did not succeed, however, in preparing condensation compounds when acetone was replaced by its homologues. Scheiber and Wolf (*Annalen*, 1908, **357**, 25), who studied the reaction products of acetone and these β-arylhydroxylamines in some detail, suggested that the condensation is due to loss of water following direct combination of the two reagents; *e.g.*,



$$2\mathrm{CMe_2}<\begin{matrix}\mathrm{OH}\\ \mathrm{NPh\cdot OH}\end{matrix} \longrightarrow \mathrm{O}<\begin{matrix}\mathrm{NPh\cdot CMe_2}\\ \mathrm{NPh\cdot CMe_2}\end{matrix}>\mathrm{O} \quad \text{or} \quad \mathrm{O}<\begin{matrix}\mathrm{NPh\cdot CMe_2}\\ \mathrm{CMe_2\cdot NPh}\end{matrix}>\mathrm{O}.$$

They did not, however, prepare any crystalline derivatives or well-defined decomposition products in support of either of these formulæ.

Although, as stated by Scheiber and Wolf (*loc. cit.*), the condensation product of β-phenylhydroxylamine and acetone is very susceptible to acidic reagents, yet it is possible by working under carefully regulated conditions to prepare a number of its crystalline derivatives and other definitely characterised products. The formation of these is in no way accounted for by the formulæ given above.

The maximum yield of the condensation product—68%—is obtained by the interaction, at the ordinary temperature, of dry β-phenylhydroxylamine and acetone during a period of two to three months. Reaction at a higher temperature results in rapid decomposition of the β-phenylhydroxylamine, and the effect of adding calcium chloride or sodium sulphate to the reaction mixture to combine with the liberated water is to diminish the yield of the condensation product.

The filtrate after removal of the condensation product consists of two layers: (*a*) water, (*b*) an acetone solution of azoxybenzene and aniline. The latter two substances are the normal decomposition products of β-phenylhydroxylamine and can be isolated in amounts almost sufficient to account for the portion of the β-phenylhydroxylamine which does not condense with acetone. The probable course of the reaction between acetone and β-phenylhydroxylamine may therefore be represented by the equation $2\mathrm{Me_2CO} + 2\mathrm{PhNH\cdot OH} = \mathrm{C_{18}H_{22}O_2N_2} + 2\mathrm{H_2O}$.

The condensation product decomposes slowly in solution at the ordinary temperature; when a solution in 96% alcohol is boiled for 24 hours, complete decomposition into mesityl oxide, aniline, and azoxybenzene occurs.

The condensation product reacts readily at the ordinary temperature with acetic anhydride to yield a crystalline *monoacetyl* derivative, $C_{20}H_{24}O_3N_2$, and in pyridine solution with benzoyl chloride to give a crystalline *monobenzoyl* derivative, $C_{25}H_{26}O_3N_2$. These results alone suffice to show the incorrectness of the formulæ mentioned above, since none of them contains a reactive hydrogen atom which would be likely to undergo displacement by an acyl group. The acyl derivatives are readily and quantitatively converted into the original condensation product on hydrolysis and therefore are very probably derivatives of it and not of some transformation compound.

The introduction of an acyl group into the molecule of the condensation product renders it resistant to permanganate and other oxidising agents and to dilute acids—including acetic acid—which attack it readily. The acyl group evidently protects a very reactive portion of the molecule, and since it can be removed by warming for a few minutes with alcoholic potash, there is a strong presumption that the group so protected is a hydroxyl group. Additional evidence for the presence of a hydroxyl group is afforded by the production at the ordinary temperature of a *potassium* derivative, $C_{18}H_{21}O_2N_2K$, which reacts with benzoic anhydride to give the benzoyl derivative described above. That the hydroxyl group is attached to nitrogen is rendered probable by the ease with which this potassium derivative is quantitatively oxidised by air to a red *compound*, $C_{18}H_{21}O_2N_2$ (see p. 1622).

Action of Dilute Hydrochloric Acid on the Condensation Product.—The finely-powdered material is readily decomposed by dilute hydrochloric acid, the principal product being a liquid *base*, $C_{12}H_{16}ONCl$; small quantities of azobenzene, β-phenylhydroxylamine and *p*-chloroaniline and a trace of mesityl oxide are also produced. This base differs in composition from the original compound by C_6H_6ONCl, and this fact and the nature of the by-products indicate that one of the β-phenylhydroxylamine residues has been detached from the compound during the reaction. Moreover, the acquisition of a chlorine atom under such mild treatment is in harmony with the view that a hydroxyl group attached to a nitrogen atom has been replaced by a chlorine atom : $\cdot NPh\cdot OH + HCl \longrightarrow \cdot NPhCl$. The chloro-base thus produced does not, however, liberate iodine from an acidified solution of potassium iodide, so it is necessary to assume that the chlorine atom has already migrated into the benzene nucleus. This view is confirmed by the behaviour of the chloro-base, which decomposes into *p*-chloroaniline and mesityl oxide in molecular proportions on heating and gives equivalent quantities of *p*-chloroacetanilide and mesityl oxide by interaction with acetic anhydride. Moreover, it reacts with nitrous acid to give a yellow crystalline *nitrosoamine* (m. p. 75—76°)—a result which further supports the view that the chlorine atom has wandered * from the nitrogen atom to the nucleus.

The production of mesityl oxide and *p*-chloroaniline in equivalent proportions accounts entirely for the molecule of the chloro-base—$C_{12}H_{16}ONCl = C_6H_{10}O + C_6H_6NCl$—and several attempts have been made, though unsuccessfully, to synthesise it from these two compounds.

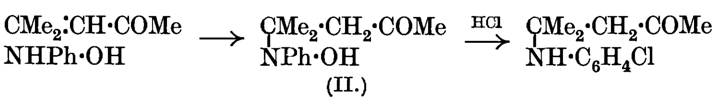
The chloro-base readily yields a crystalline *semicarbazone* ($C_{13}H_{19}ON_4Cl$), the oxygen atom thus being shown to be ketonic, and by its reduction with sodium and alcohol sodium chloride and aniline are obtained in equivalent quantities together with *p*-chloroaniline and methyl*iso*butylcarbinol. There can be little doubt, therefore, that the constitution of the chloro-base is represented by formula (I), and its modes of decomposition by heat and by acetic anhydride by the scheme :

$$\begin{array}{ll} \underset{\text{(I.)}}{C_6H_4Cl{\cdot}NH{\cdot}CMe_2{\cdot}CH_2{\cdot}COMe} & \xrightarrow{\text{heat}} CMe_2{:}CH{\cdot}COMe + C_6H_4Cl{\cdot}NH_2. \\ \quad\quad\quad\quad \big\lfloor \xrightarrow{Ac_2O} & CMe_2{:}CH{\cdot}COMe + C_6H_4Cl{\cdot}NHAc + AcOH. \end{array}$$

Its formation from the original compound can be represented by the equation :

$$C_{18}H_{22}O_2N_2 + HCl = C_6H_4Cl{\cdot}NH{\cdot}CMe_2{\cdot}CH_2{\cdot}COMe + NHPh{\cdot}OH.$$

The constitution of the chloro-base as β-p-*chloroanilino*-β-*methylpentan*-δ-*one* has been established by its synthesis from β-phenylhydroxylamine and mesityl oxide by the following reactions :



$$\begin{array}{l} CMe_2{:}CH{\cdot}COMe \\ NHPh{\cdot}OH \end{array} \longrightarrow \begin{array}{l} CMe_2{\cdot}CH_2{\cdot}COMe \\ | \\ NPh{\cdot}OH \end{array} \xrightarrow{HCl} \begin{array}{l} CMe_2{\cdot}CH_2{\cdot}COMe \\ | \\ NH{\cdot}C_6H_4Cl \end{array}$$

(II.)

The compound (II) is too unstable to be isolated ; its *sodium* derivative, however, has been prepared by the interaction of mesityl oxide and the sodium derivative of β-phenylhydroxylamine.

The complete and facile scission, by the action of dilute hydrochloric acid, of a molecule of β-phenylhydroxylamine from the original condensation product renders it probable that the latter is β-*phenyl*-

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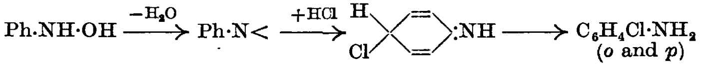
* The mechanism of the formation of *p*-chloroaniline from β-phenylhydroxylamine and hydrochloric acid is represented by Bamberger (*Ber.*, 1900, **33**, 3600; 1901, **34**, 61) as follows :

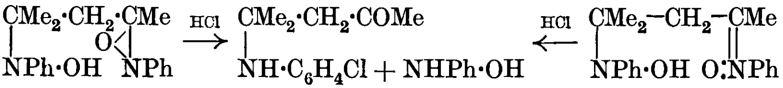


and by Löb (*Ber.*, 1896, **29**, 1894) as

$$Ph{\cdot}NH{\cdot}OH + HCl \longrightarrow Ph{\cdot}NHCl \longrightarrow C_6H_4Cl{\cdot}NH_2.$$

The experimental results recorded above are clearly opposed to Bamberger's view and in agreement with Löb's.

hydroxylamino-β-methylpentan-δ-oneoxime N-*phenyl ether* (III), or *β-phenylhydroxylamino-β-methylpentane-δ-phenylimine oxide* (IV), and its interaction with hydrochloric acid may be represented thus :

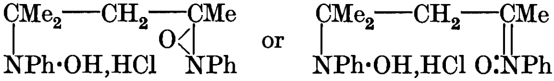


$$\begin{array}{l}\text{CMe}_2\cdot\text{CH}_2\cdot\text{CMe}\\ |\qquad\quad \text{O}\langle|\\ \text{NPh}\cdot\text{OH}\quad\text{NPh}\end{array} \xrightarrow{\text{HCl}} \begin{array}{l}\text{CMe}_2\cdot\text{CH}_2\cdot\text{COMe}\\ |\\ \text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}+\text{NHPh}\cdot\text{OH}\end{array} \xleftarrow{\text{HCl}} \begin{array}{l}\text{CMe}_2-\text{CH}_2-\text{CMe}\\ |\qquad\qquad\quad ||\\ \text{NPh}\cdot\text{OH}\ \ \text{O}\!:\!\text{NPh}\end{array}$$

(III.) (IV.)

This view of the constitution of the condensation product is supported by the following additional reactions. The condensation product is rapidly decomposed by hot concentrated hydrochloric acid, giving mesityl oxide (20·5%), *p*-chloroaniline (33%) and azoxybenzene (16%) together with a small amount of a substance of very high boiling point. A similar decomposition is effected by steam, the principal products being azoxybenzene, mesityl oxide, and tarry material which has not been identified. When heated with an alcoholic solution of zinc chloride, the condensation product decomposes into *p*-phenetidine, azoxybenzene, *p*-chloroaniline, aniline and mesityl oxide. A similar scission of the molecule is brought about by the prolonged action of cold dilute sulphuric acid, the products being *p*-aminophenol, mesityl oxide and azoxybenzene; these can be isolated in amounts which account for 80% of the original material.

In marked contrast to the above-mentioned hydrolytic agents, hydrogen chloride converts the condensation product in dry ethereal solution into its *monohydrochloride*, a white solid which is decomposed by water into its components. This compound resembles β-phenylhydroxylamine hydrochloride in its behaviour and its constitution is probably



$$\begin{array}{l}\text{CMe}_2\text{---CH}_2\text{---CMe}\\ |\qquad\qquad\qquad \text{O}\langle|\\ \text{NPh}\cdot\text{OH,HCl}\quad\text{NPh}\end{array} \quad\text{or}\quad \begin{array}{l}\text{CMe}_2\text{---CH}_2\text{---CMe}\\ |\qquad\qquad\qquad\ \ ||\\ \text{NPh}\cdot\text{OH,HCl}\ \text{O}\!:\!\text{NPh}\end{array}$$

Reduction of the Condensation Product.—The condensation product is unaffected in moist ethereal solution by aluminium amalgam. It is, however, readily reduced in absolute alcoholic solution by sodium; aniline, azobenzene, and methyl*iso*butylcarbinol are formed, but the main product is a secondary *base*, $C_{12}H_{19}ON$, from which a *chloroplatinate*, a yellow, crystalline *nitrosoamine*, and a *diacetyl* derivative have been prepared. Since one of the acetyl groups in this derivative is much more easily removed by hydrolysis than the other, it is probable that the secondary base contains a hydroxyl group. Two formulæ for this compound suggest themselves:

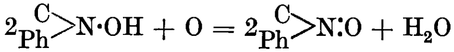
$$\mathrm{NHPh{\cdot}CMe_2{\cdot}CH_2{\cdot}CHMe{\cdot}OH} \quad \text{and} \quad \mathrm{CHMe_2{\cdot}CH_2{\cdot}CMe(OH){\cdot}NHPh},$$

of which the former is the more probable, as it implies a decomposition of the condensation product similar to that brought about by hydrolytic agents. The alternative formula is improbable, since a compound of this structure would tend to be dehydrated by an excess of an acetylating agent.

Several unsuccessful attempts were made to synthesise the secondary base from aniline and mesityl oxide. The only definite compound which could be isolated appeared to be produced by the condensation of one molecule of mesityl oxide with two molecules of aniline.

Action of Oxidising Agents on the Condensation Product.—When the finely powdered condensation product is agitated with a solution of potassium permanganate, potassium ferricyanide, sodium hypobromite, or ammoniacal silver oxide, or is exposed, suspended in faintly alkaline water, to the air for several weeks, it is oxidised to a bright red, crystalline compound. The most convenient procedure, however, is by the use of ammoniacal silver oxide as described in the experimental section. The oxidised compound, which is easily obtained pure in a yield of 98% of the theoretical amount, is produced by the action of one-half molecular quantity of silver oxide, it thus being shown that only one atom of hydrogen is removed from each molecule of the condensation product. Its molecular weight is of the same order of magnitude (about 300) as that of the unoxidised compound and therefore there has been no condensation between two molecules of the latter with the elimination of hydrogen. Moreover, the two compounds are almost identical in composition and therefore no oxygen has entered the original substance. That no change other than oxidation occurs during the reaction is shown by the quantitative regeneration of the original compound by the action of aluminium amalgam on a cold moist ethereal solution of the red oxidation compound.

The oxidised and the unoxidised compound differ in several important properties. The former does not react with acetic anhydride or with benzoyl chloride in pyridine solution at the ordinary temperature, the absence of a hydroxyl group being thus indicated. This view is supported by the marked difference in the behaviour of cold dilute hydrochloric acid towards the two compounds; whereas the oxidised compound is unaffected by this reagent (and other cold dilute mineral acids), the unoxidised one undergoes an immediate change involving the substitution of one atom of chlorine for one atom of hydrogen and one of oxygen—a type of reaction to which β-arylhydroxylamines are peculiarly susceptible. It is therefore probable that the oxidation process involves the reaction

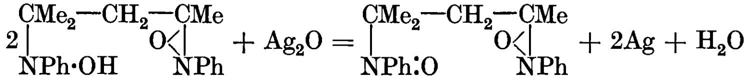


$$2\,{}^{\mathrm{C}}_{\mathrm{Ph}}\!>\!\mathrm{N{\cdot}OH} + \mathrm{O} = 2\,{}^{\mathrm{C}}_{\mathrm{Ph}}\!>\!\mathrm{N{:}O} + \mathrm{H_2O}$$

and leads to the production of a compound which contains a quadrivalent nitrogen atom.

Additional support for this view is furnished by the following experimental evidence : (*a*) one of the hydrolytic products of the action of dilute hydrochloric acid on the original condensation compound is β-phenylhydroxylamine (see p. 1623), whilst the oxidised compound in dry ethereal solution combines with hydrogen chloride to give a derivative the decomposition of which by water yields 50% of the unoxidised compound and 10% of nitrosobenzene (*i.e.*, oxidised β-phenylhydroxylamine); (*b*) the oxidised compound is immediately decomposed by steam, giving a mixture of products from which the original unoxidised compound (22%) and nitrosobenzene (13%) can be isolated; (*c*) when the oxidised compound is gently heated under diminished pressure, it decomposes and nitrosobenzene sublimes from the reaction products.

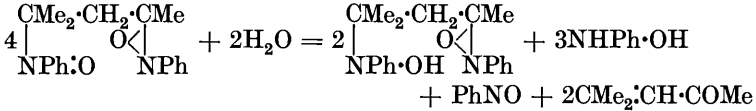
Since both the unoxidised and the oxidised compound yield under the action of hot dilute mineral acids, or even of hot water, considerable quantities of mesityl oxide, the structural similarity of the aliphatic portions of the two molecules is confirmed. The oxidation process may therefore be expressed by the equation



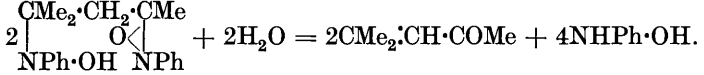
$$2\begin{array}{l}\mathrm{CMe_2{-}CH_2{-}CMe}\\ \big|\qquad\qquad\ \ \mathrm{O}\!<\!\big|\\ \mathrm{NPh{\cdot}OH}\qquad \mathrm{NPh}\end{array} + \mathrm{Ag_2O} = \begin{array}{l}\mathrm{CMe_2{-}CH_2{-}CMe}\\ \big|\qquad\qquad\ \ \mathrm{O}\!<\!\big|\\ \mathrm{NPh{:}O}\qquad\ \ \mathrm{NPh}\end{array} + 2\mathrm{Ag} + \mathrm{H_2O}$$

β(phenylnitrogen oxide)-β-methylpentane-δ-oneoxime *N*-phenyl ether.

and the decomposition of the two compounds by the equations



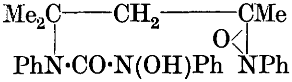
$$4\begin{array}{l}\mathrm{CMe_2{\cdot}CH_2{\cdot}CMe}\\ \big|\qquad\quad\ \mathrm{O}\!<\!\big|\\ \mathrm{NPh{:}O}\quad\ \ \mathrm{NPh}\end{array} + 2\mathrm{H_2O} = 2\begin{array}{l}\mathrm{CMe_2{\cdot}CH_2{\cdot}CMe}\\ \big|\qquad\quad\ \mathrm{O}\!<\!\big|\\ \mathrm{NPh{\cdot}OH}\ \mathrm{NPh}\end{array} + 3\mathrm{NHPh{\cdot}OH} + \mathrm{PhNO} + 2\mathrm{CMe_2{:}CH{\cdot}COMe}$$



$$2\begin{array}{l}\mathrm{CMe_2{\cdot}CH_2{\cdot}CMe}\\ \big|\qquad\quad\ \mathrm{O}\!<\!\big|\\ \mathrm{NPh{\cdot}OH}\ \mathrm{NPh}\end{array} + 2\mathrm{H_2O} = 2\mathrm{CMe_2{:}CH{\cdot}COMe} + 4\mathrm{NHPh{\cdot}OH}.$$

The experimental results so far recorded do not enable a decision to be made between the oxime-ether and the nitrone formulations of the condensation compound. The following results are in harmony with the first view, but since the evidence is of a negative character the question is not considered settled. Attempts are being made to obtain further evidence on this point.

The condensation product forms an additive compound with phenylcarbimide (1 mol.)—a result which is not obtained with either its acetyl derivative or its oxidation product. All the experimental evidence points to these two derivatives having the same molecular structure as the parent compound with the sole modification that a >N·OH group has been converted in the one case into >N·O·CO·CH_3 and in the other into >N⁚O. It is highly probable, therefore, that phenylcarbimide reacts with the >N·OH part of the condensation product to give a compound



$$\begin{array}{lll} \mathrm{Me_2C} & \text{———}\ \mathrm{CH_2}\ \text{———} & \mathrm{CMe} \\ \quad | & \qquad\qquad \mathrm{O}\!\lt & | \\ \mathrm{PhN{\cdot}CO{\cdot}N(OH)Ph} & & \mathrm{NPh} \end{array}$$

which is analogous to β-carbanilino-β-phenylhydroxylamine, NHPh·CO·N(OH)Ph, produced by the interaction of phenylcarbimide and β-phenylhydroxylamine (Beckmann, *J. pr. Chem.*, 1897, **56**, 71).

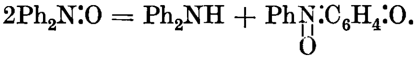
It follows also that there is present in the condensation product no other group capable of reacting with phenylcarbimide.

Evidence for the view that the condensation products of β-phenylhydroxylamine with acetone and with benzaldehyde differ in structure is the fact that the latter product is unaffected by cold concentrated hydrochloric acid or 65% sulphuric acid, reagents which hydrolyse the acetone compound with the greatest readiness.

One of the very few recorded cases of organic compounds which contain quadrivalent nitrogen is diphenylnitric oxide, which Wieland and Offenbächer (*Ber.*, 1914, **47**, 2111) obtained by the oxidation of ββ-diphenylhydroxylamine with silver oxide:

$$2\mathrm{Ph_2N{\cdot}OH} + \mathrm{O} = 2\mathrm{Ph_2N{:}O} + \mathrm{H_2O} \quad . \quad . \quad . \quad (1)$$

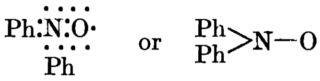
Diphenylnitric oxide is described as an intensely red substance which decomposes on keeping; liberates iodine from an acidified solution of potassium iodide; is reduced by phenylhydrazine to the original ββ-diphenylhydroxylamine and by stronger reducing agents to diphenylamine; and is converted by the action of dilute hydrochloric acid, by simultaneous oxidation and reduction, into diphenylamine and quinoneanil oxide—a change which sometimes occurs spontaneously in ethereal solution (Wieland and Roth, *Ber.*, 1920, **53**, 215):



$$2\mathrm{Ph_2N{:}O} = \mathrm{Ph_2NH} + \mathrm{Ph}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{N}}\mathrm{{:}C_6H_4{:}O}.$$

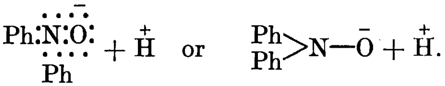
There are, therefore, many points of similarity between diphenylnitric oxide and the red compound formed by the oxidation of the condensation product of β-phenylhydroxylamine and acetone, in which the presence of a quadrivalent nitrogen atom has been suggested.

The formulation of the oxidation of diphenylhydroxylamine to diphenylnitric oxide as in equation (1) is in conflict with the electronic theory. The reaction is, however, of some interest, since the oxygen atom which takes part in the reaction gains two electrons and acquires them from two molecules of the hydroxylamine. Obviously, therefore, each molecule of diphenylhydroxylamine loses one electron, and the product of oxidation has, according to the electronic theory, the formula



$$\mathrm{Ph{:}\underset{Ph}{\overset{\cdot\cdot\cdot\cdot}{\underset{\cdot\cdot\cdot\cdot}{N{:}O\cdot}}}}\quad\text{or}\quad \begin{matrix}\mathrm{Ph}\\\mathrm{Ph}\end{matrix}\!\!>\mathrm{N{-}O}$$

and can be contrasted with diphenylhydroxylamine which has "ionised":



$$\mathrm{Ph{:}\underset{Ph}{\overset{\cdot\cdot\cdot\cdot}{\underset{\cdot\cdot\cdot\cdot}{N{:}O{:}}}}}^{-}+\overset{+}{\mathrm{H}}\quad\text{or}\quad \begin{matrix}\mathrm{Ph}\\\mathrm{Ph}\end{matrix}\!\!>\mathrm{N{-}}\overset{-}{\mathrm{O}}+\overset{+}{\mathrm{H}}.$$

The particular type of N—O compound formed by the oxidation of the condensation product of acetone and phenylhydroxylamine belongs, therefore, to the small class of substances whose molecules contain an uneven number of electrons—the so-called "odd electron molecules"—of which nitrogen dioxide is the most typical example; others are nitric oxide, triphenylmethyl, and chlorine dioxide. Lewis states that "odd electronic compounds" with the exception of nitric oxide absorb light in the visible part of the spectrum and are generally intensely coloured. They are very reactive and attach themselves to a great variety of substances; they tend to react in such a manner that one molecule gains an electron while another loses one (simultaneous oxidation and reduction). The red oxidation product thus appears to possess the properties of an odd electron compound, and, indeed, its method of preparation combined with the determination of its molecular weight proves that it is such a substance.

EXPERIMENTAL.

Preparation of the Condensation Product.—β-Phenylhydroxylamine, prepared by Kamm's method ("Organic Syntheses," IV, 57) in 60% yield, was dissolved in rather more than its own weight of dry acetone, and the filtered solution was kept for several days at room temperature; the condensation product then began to crystallise. Thereafter the mixture was kept, with daily agitation, in the ice-chest for 3 months, until no further separation occurred. The yield of the condensation product varied from 40—68% (calculated on the amount of β-phenylhydroxylamine), the better yields being obtained when carefully dried β-phenylhydroxylamine was used. The condensation product, after being washed with cold acetone, in which it was only slightly soluble, was obtained almost colourless. It crystallised from ethyl alcohol in hard, glassy rhombs, m. p. 136° (slight decomp.). In a typical experiment, 5704 g. of β-phenylhydroxylamine dissolved in acetone (6830 c.c.) gave, after several weeks, 3719 g. of the condensation product (yield 49%).

The reaction mixture, when left undisturbed and "unseeded," deposits the condensation product in large, colourless, transparent, glassy rhombs which remain colourless and retain the same melting point (136°) for several years. The small crystals obtained by frequent agitation of the solution slowly develop, during several months, a pale yellow colour and a slight odour: this is probably due to their retaining a small quantity of the mother-liquor.

Earlier workers state that this compound melts with decomposition. The amount of decomposition, however, is very small, for a molten sample will resolidify and then melt at a temperature only a few degrees below the original melting point; after one crystallisation from alcohol, it melts at 136°.

The Acetyl Derivative.—(a) To the deep brownish-orange solution obtained by shaking the finely powdered condensation product (10 g.) with pure acetic anhydride (10 c.c.) below 35°, ice is gradually added; the whole then sets to a crystalline mass. The washed and dried product (12 g.) melts at 95—97°.

(b) To a solution of the condensation product (45 g.) in pyridine (60 c.c.) acetic anhydride is added (23 c.c.) at such a rate that the temperature does not rise above 45°. After a few minutes, crushed ice is added, and the crude acetyl derivative washed and dried as before (yield, about 54 g.).

The *acetyl* derivative separates from ethyl acetate, acetone, or aqueous alcohol in radiating clusters of prismatic needles, m. p. 99—101°. When it is added to warm benzene a cloudy solution is produced which becomes clear on the addition of calcium chloride. This solution, when diluted with warm light petroleum, deposits stout needles. These melt at 105—106° (without decomp.), but at about 140° vigorous decomposition sets in and tarry products are formed (Found in material crystallised from alcohol: C, 66·95; H, 7·2; N, 7·7; $CH_3{\cdot}CO$, 12·6. $C_{20}H_{24}O_3N_2,H_2O$ requires C, 67·0; H, 7·3; N, 7·8; $CH_3{\cdot}CO$, 12·0%. Found in material crystallised from benzene : C, 71·0; H, 7·1; *M*, cryoscopic in benzene, 310. $C_{20}H_{24}O_3N_2$ requires C, 70·6; H, 7·1%; *M*, 340).

The acetyl derivative was recovered unchanged after 1 g. had been heated with acetic anhydride (3 c.c.) at 100° for 10 minutes.

The Benzoyl Derivative.—(a) A solution of the condensation product (12 g.) and benzoyl chloride (6 g.) in pyridine (50 c.c.) is, after several hours, mixed with crushed ice. The washed and dried crystalline product, m. p. 90—95°, is obtained in almost quantitative yield.

(b) A suspension of the potassium derivative of the condensation product (see below) in pure dry ether is shaken with benzoic anhydride (1 mol.) for 15 minutes, the gelatinous precipitate of potassium benzoate filtered off and washed with dry ether, and the filtrate concentrated; the benzoyl derivative is thus obtained as an orange oil which solidifies completely on inoculation.

The *benzoyl* derivative crystallises from aqueous alcohol in rosettes of glistening, prismatic needles, m. p. 96—98°, containing $1H_2O$ (Found : C, 71·0; H, 6·9; N, 6·6. $C_{25}H_{26}O_3N_2,H_2O$ requires C, 71·4; H, 6·7; N, 6·7%) and from benzene or light petroleum in anhydrous, prismatic needles, m. p. 98—99° (Found : C, 74·6; H, 6·4. $C_{25}H_{26}O_3N_2$ requires C, 74·6; H, 6·4%).

Hydrolysis. To a solution of the benzoyl derivative (1·1 g.) in warm alcohol (10 c.c.), sodium hydroxide (0·2 g.) was added, followed, after 10 minutes, by water. The crystalline product, m. p. 135—136°, weighed 0·62 g. (calc., 0·78 g.) and from the concentrated acidified filtrate 0·25 g. of benzoic acid was obtained (calc., 0·32 g.).

The *potassium* derivative is prepared by adding a benzene solution of the condensation product to rather less than one atomic proportion of finely powdered potassium. The latter dissolves, hydrogen is evolved, the liquid darkens, and a white gelatinous precipitate forms. This is filtered off, washed quickly with dry benzene several times, and dried in a vacuum (Found : K, 11·7, 11·8. $C_{18}H_{21}O_2N_2K$ requires K, 11·3%). When left for several days in a dry atmosphere, the substance (1·1 g.) develops an orange colour and, on treatment with water, gives an orange powder, m. p. about 90°. After crystallisation from alcohol, this powder is obtained in fine red needles (1·0 g.); these, alone or mixed with an authentic specimen of the red oxidation product, melt at 89—90°.

By passing hydrogen chloride into a dry ethereal solution of the condensation product, its *monohydrochloride* is obtained as a white solid which, after being washed with ether and dried in a vacuum, melts at 62—64° and at 80° undergoes vigorous decomposition

(Found : HCl, 11·1. $C_{18}H_{22}O_2N_2$,HCl requires HCl, 10·9%). The solid is stable in a vacuum for some hours, but on exposure to air turns black. It is decomposed by water with regeneration of the original condensation product in an almost pure condition.

Formation of β-p-*Chloroanilino*-β-*methylpentan*-δ-*one from the Condensation Product.*—The freshly recrystallised and finely powdered condensation product (50 g.) is shaken for 2 hours with *N*-hydrochloric acid (400 c.c.). The pale yellow solution is filtered from undissolved material (4—8 g.) and extracted three times with ether to remove azoxybenzene, mesityl oxide and a small quantity of β-phenylhydroxylamine. The acid solution is rendered alkaline and the precipitated bases (35—40 g.), after extraction and drying, are distilled under 15 mm. pressure. Two main fractions are obtained, (i) up to 150°, (ii) 150—180°. The first contains water (if the receiver has been cooled in ice), mesityl oxide, *p*-chloroaniline, and a proportion of the higher-boiling base. The second fraction, which weighs about three times as much as the first and contains the *chloro-base,* is dissolved in ether and the solution is washed with successive small quantities of dilute hydrochloric acid; thereafter a mixture (4·8 g.) of azobenzene and azoxybenzene (1 : 4) is obtained from it. The hydrochloric acid solution is rendered alkaline, the precipitated chloro-base (20 g.) is extracted with ether and twice redistilled, and a fraction collected at 169—172°/11 mm. or at 133—136° under the pressure attained with a mercury vapour pump. It is a golden-yellow liquid which shows no tendency to solidify (Found : C, 63·5; H, 7·3; N, 6·3; Cl, 15·7. $C_{12}H_{16}ONCl$ requires C, 63·8; H, 7·1; N, 6·2; Cl, 15·7%). The *nitrosoamine,* obtained by means of sodium nitrite and ice-cold, dilute hydrochloric acid, crystallises from ether–petrol in rosettes of pale yellow needles, m. p. 75—76° after softening at 70° (Found : N, 11·2. $C_{12}H_{15}O_2N_2Cl$ requires N, 11·0%).

The chloro-base readily yields a *semicarbazone,* which crystallises from alcohol in microscopic, flat prisms, m. p. 125° (Found : N, 20·2. $C_{13}H_{19}ON_4Cl$ requires N, 19·8%).

Action of Sodium and Alcohol on the Chloro-base.—To a solution of the base (5 g.) in warm alcohol, sodium (3 g.) is added in small pieces; a precipitate of sodium chloride forms. By working up the product in the usual way, there is obtained a non-basic fraction (1·7 g.), b. p. 128—133°, with a camphoraceous odour; this, after treatment with semicarbazide to remove a little unreduced mesityl oxide as its semicarbazide semicarbazone (m. p. 220°), distils at 130—134° and reacts with *p*-nitrobenzoyl chloride in pyridine solution to give a crystalline *p*-nitrobenzoic ester which melts at 24—26° either alone or when mixed with methyl*iso*butylcarbinyl *p*-nitrobenzoate. The basic portion of the product consists of unchanged chloro-base (0·5 g.), *p*-chloroaniline (1·0 g.), and aniline (0·9 g.). The chlorine present as sodium chloride in the aqueous portion, estimated volumetrically, is 0·36 g., corresponding to 0·93 g. of aniline. The substance therefore contains one aniline residue for each atom of chlorine present in the molecule.

Decomposition of β-p-*Chloroanilino*-β-*methylpentan*-δ-*one by Acetic Anhydride*.—The chloro-base (1·5 g.) is warmed for 15 minutes with an equal weight of acetic anhydride, and the cooled reaction mixture diluted with water (60 c.c.). The crystalline solid, after being washed and dried (0·96 g.), melts at 172—174°, alone or mixed with *p*-chloroacetanilide (Found : N, 8·2. Calc. : N, 8·1%). The filtrate contains a few globules of mesityl oxide (b. p. 126—130°).

Synthesis of β-p-*Chloroanilino*-β-*methylpentan*-δ-*one*.—(a) A solution of β-phenylhydroxylamine (168 g.) and mesityl oxide (148 g.) in just sufficient dry ether is kept for a month and then shaken for 3 hours with *N*-hydrochloric acid (400 c.c.). The acid layer is separated, extracted three times with ether, and rendered alkaline with sodium hydroxide, and the precipitated base is extracted, dried, and distilled; the principal fraction, b. p. 160—175°/15 mm., gives, after four distillations, a fraction (40 g.), b. p. 172—175°/13 mm. (Found: N, 6·3; Cl, 15·7. Calc. for $C_{12}H_{16}ONCl$: N, 6·2; Cl, 15·7%). During distillation the base undergoes slight decomposition into mesityl oxide and *p*-chloroaniline.

The semicarbazone, prepared in the usual manner, crystallises from alcohol in microscopic, flat prisms, m. p. 124—125°.

(b) The gelatinous sodium derivative of β-phenylhydroxylamine obtained from sodium (1 equiv.) and phenylhydroxylamine (20 g.) in dry ethereal solution dissolves on addition of mesityl oxide (1 mol.), heat is developed, and a precipitate slowly separates. After 10 days, this is filtered off, quickly washed with dry ether, and dried (wt. 10 g.) (Found: Na, 11·5. $C_{12}H_{16}O_2NNa$ requires Na, 10·0%). The compound evidently contains unchanged sodium derivative of β-phenylhydroxylamine (Na, 17·6%). It is very hygroscopic and decomposes on standing. It is decomposed by water, and the liberated compound is converted by cold dilute hydrochloric acid into β-*p*-chloroanilino-β-methylpentan-δ-one. This synthetic chloro-base yields a semicarbazone which melts at 125° either alone or when mixed with the semicarbazone of the chloro-base obtained by the action of dilute hydrochloric acid on the original condensation compound. Acetic anhydride decomposes it into mesityl oxide and *p*-chloroacetanilide.

Behaviour of the Condensation Product.—(a) *Towards hot hydro-*

chloric acid. A current of steam is passed into a mixture of the condensation product (100 g.) and concentrated hydrochloric acid (100 c.c.); rapid decomposition takes place and mesityl oxide (20·5 g.) distils with the steam. From the non-volatile product, *p*-chloroaniline (33 g.), azoxybenzene (16 g.), and a non-basic material of high boiling point (2 g.) are obtained.

(b) *Towards steam.* A rapid current of steam is passed over the finely powdered compound (20 g.). An oil distils with the first 6 l. of water, leaving a black tar (5 g.). The oil sets, on cooling, to a crystalline mass of azoxybenzene (9·7 g.). Extraction of the aqueous distillate yields mesityl oxide (2·5 g.).

(c) *Towards an alcoholic solution of zinc chloride.* Zinc chloride (50 g.), the condensation product (50 g.), and ethyl alcohol (250 c.c.) are heated together under reflux for 30 minutes. After cooling, the crystalline material is filtered off and recrystallised from alcohol, glistening leaflets (9·2 g.), m. p. 237—239°, of p-*phenetidine zincichloride* being obtained [Found: Zn, 15·6; Cl, 17·4; C, 46·3; H, 5·7. $(EtO{\cdot}C_6H_4{\cdot}NH_2)_2,ZnCl_2$ requires Zn, 15·8; Cl, 17·2; C, 46·6; H, 5·3%]. From the mother-liquor, aniline (2 g.), *p*-chloroaniline (10 g.), azoxybenzene * (11·5 g.), and mesityl oxide (3 g.) are isolated. Much of the last substance is undoubtedly lost owing to its low boiling point (40°) at the pressure employed.

The zincichloride yields phenacetin when it is heated with acetic anhydride, and *p*-phenetidine hydrochloride, m. p. 236—237°, when heated with hydrochloric acid.

Preparation of the Red Oxidation Compound.—A mixture of the finely powdered condensation product (59·6 g.), light petroleum, b. p. 40—60° (1500 c.c.), and an ammoniacal solution of silver oxide (from 36 g. of silver nitrate) is mechanically shaken for 48 hours; oxidation commences almost at once, the petroleum solution turning bright red and metallic silver being deposited. The petroleum layer is separated from the filtered liquid, washed with water, dried, and evaporated slowly in a bath of warm water (to avoid overheating), until crystallisation sets in. The solid on the filter is washed with water until free from ammonia, air-dried, and repeatedly extracted with dry ether; the extracts are evaporated to small bulk and diluted with light petroleum until crystallisation sets in. About one-third of the oxidation product is contained in the original petroleum solution, the remainder having crystallised

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* It is stated in the literature (Meyer and Jacobson, "Organische Chemie," II, 251; Beilstein, "Organische Chemie," IV, 1335) that azoxybenzene decomposes on heating. We have found that it distils quite readily at 191°/12 mm. with only slight decomposition. The pale yellow distillate sets completely to a mass of long, hair-like needles, m. p. 35°.

and become mixed with the metallic silver. The yield is 58·4 g. (98% of the theoretical).

This substance crystallises from petroleum in compact, hemispherical clusters of bright red, glistening prisms which melt and decompose at 88—90°, producing a black liquid which does not resolidify [Found: C, 72·7; H, 7·15; N, 9·4; *M*, cryoscopic in benzene, 276 (mean of four values). $C_{18}H_{21}O_2N_2$ requires C, 72·7; H, 7·1; N, 9·4%; *M*, 297].

Determinations of the molecular weight of the oxidised compound in acetone by the ebullioscopic method gave values ranging from 285 to 325, but little reliance can be placed upon these, as some decomposition occurred in the hot solution. After evaporation of the acetone, the residue had a strong odour of nitrosobenzene and contained crystals of the original unoxidised condensation product of m. p. 135—136°.

Reactions of the Red Oxidation Compound.—(a) *Reduction.* The compound in ethereal solution is quantitatively reduced to the original condensation product by (*a*) zinc dust and dilute caustic soda solution, (*b*) aluminium amalgam, (*c*) phenylhydrazine. The product melts at 133—136° and 136° before and after crystallisation, respectively.

By the action of potassium iodide and dilute acetic acid on an ethereal solution of the oxidation compound the original condensation product is obtained in 77% yield, the remaining material being a dark, thick oil from which nothing crystalline can be isolated.

(b) *Action of heat.* A rapid current of steam is passed over the oxidation compound (10 g.). Fusion and decomposition take place at once and nitrosobenzene (1·2 g.) passes over with the steam. From the non-volatile portion there are isolated the original condensation product (2·2 g.), azoxybenzene (2 g.), and tar. A similar decomposition is brought about at lower temperatures when a solution of the oxidation compound in acetone is heated under reflux for several hours; the original condensation product is obtained in a yield of about 50%.

(c) *Action of acylating agents.* (i) A mixture of acetic anhydride (8 c.c.) and the finely powdered oxidation compound (6 g.) is maintained at 35° for several minutes, until solution is complete. After 30 minutes, crushed ice is added to the brownish-red solution and the precipitated paste is macerated with cold water until a sandy powder (3·8 g.) with the odour of nitrosobenzene is obtained. This crystallises in colourless needles, m. p. 105—106° (from dry benzene) or 99—100° (from aqueous alcohol). Yield 50%. Analysis and mixed melting-point determinations prove that it is the acetyl derivative of the original condensation product of m. p. 136°; and it yields this on hydrolysis. A 50% yield of the same acetyl derivative is obtained by the action of acetyl chloride on a solution of the oxidation compound in pyridine.

In marked contrast to the behaviour of the original condensation product, which in pyridine solution readily gives an acetyl derivative in quantitative yield by the action of acetic anhydride, the oxidation compound is unacted upon under similar conditions at the ordinary or at a slightly raised temperature. At higher temperatures, profound decomposition sets in and unworkable tars are produced. This result clearly indicates that some prior reaction is necessary before acetylation can take place.

In a similar manner, by the action of benzoyl chloride (3 g.) on a pyridine (40 c.c.) solution of the oxidation compound (6 g.), there is obtained the benzoyl derivative of the original condensation product in 50% yield; m. p. and "mixed" m. p. 97—99°.

(d) *Action of hydrogen chloride.* Dry hydrogen chloride is rapidly absorbed by a dry ethereal solution of the oxidation compound, and an orange precipitate separates; the solution becomes colourless, but slowly turns green. If the passage of hydrogen chloride is still continued, nitrosobenzene and mesityl oxide can be isolated from the solution; but if the current is stopped when the solution becomes colourless, and the orange precipitate rapidly filtered off, washed with dry ether, and dried in a vacuum desiccator, it has the empirical formula $C_{18}H_{21}O_2N_2,2HCl$. This substance is not identical with the monohydrochloride of the original condensation product (*vide* p. 1622), but it yields this product in nearly 50% yield on treatment with water.

Action of Phenylcarbimide on the Condensation Product.—A solution of the condensation product (9 g.) and phenylcarbimide (3·3 g.; 1 mol.) in dry ether is gently warmed for 3 hours and the ether is then evaporated. The residue of colourless, cubic crystals, coated with red oil, is washed with small quantities of cold light petroleum and recrystallised from acetone, transparent, colourless cubes, m. p. 128—129° (decomp.), being thus obtained (Found: C, 71·8; H, 7·0; N, 9·7. $C_{25}H_{27}O_3N_3$ requires C, 71·8; H, 6·5; N, 10·0%). This substance is almost insoluble in cold alcohol and decomposes slightly in hot alcohol. A mixture of it with the original condensation product (m. p. 136°) melts at 104—109°.

Preparation of the Liquid Reduction Product.—To a solution of the condensation compound (60 g.) in boiling absolute ethyl alcohol (500 c.c.), sodium (23 g.) is added sufficiently quickly to keep the liquid boiling. When all the sodium has dissolved, water is added to the dark red reaction mixture and the solution is extracted several times with ether. The ethereal solution is washed with water, extracted with dilute hydrochloric acid, and evaporated to dryness; the residue is pure azobenzene. The basic material in the acid extract is recovered and repeatedly fractionally distilled under diminished pressure, being thus separated into aniline and the new *base* (15 g.), a golden-yellow, somewhat viscous liquid, b. p. 130—133°/2—4 mm. or 160—163°/15 mm., $d_{4^\circ}^{18^\circ}$ 1·0043 (Found: C, 74·8; H, 9·6; N, 7·3. $C_{12}H_{19}ON$ requires C, 74·6; H, 9·8; N, 7·25%).

Modifications of the method of reduction were tried with the object of preventing the formation of azobenzene. These included the gradual addition of sufficient acetic acid to neutralise the sodium ethoxide as it was produced—this procedure, however, caused the production of phenylcarbylamine, which was very difficult to remove on distillation. The presence of water—even 1%—in the alcohol diminishes the amount of base produced and increases the proportion of azobenzene formed even to the exclusion of the base when the quantity of water is considerable. When the absolute alcohol is replaced by amyl alcohol, no base is formed, an almost quantitative yield of azobenzene * being obtained together with a trace of aniline.

By doubling the amount of sodium used in the reduction, there was produced, in addition to the liquid base, hydrazobenzene (5 g.), which was isolated from the acid extract in the form of benzidine.

The pure base readily yields a *diacetyl* derivative, which crystallises from acetone in clusters of prismatic needles, m. p. 104—106° (Found: N, 4·9; $2CH_3\cdot CO$, 31·8; $1CH_3\cdot CO$, 19·0. $C_{16}H_{23}O_3N$ requires N, 5·05; $2CH_3\cdot CO$, 31·1; $1CH_3\cdot CO$, 15·5%). When the hydrolysis is effected by aqueous potassium hydroxide, a value for the acetyl content of 19% is quickly obtained; this value increases at only a slow rate as the heating is continued—the maximum value of 31·1% was only obtained by heating with *alcoholic* potassium hydroxide during 24 hours. It is evident, therefore, that one acetyl group is much more firmly attached than the other.

The *chloroplatinate* of the base is obtained by the addition of chloroplatinic acid (1 mol.) in alcoholic solution. The precipitate crystallises from methyl alcohol containing a small amount of hydrochloric acid in clusters of orange prisms which, after drying at 110° for 4 hours, melt and decompose at 197—198° [Found: Pt, 24·9, 24·6. $(C_{12}H_{19}ON)_2,H_2PtCl_6$ requires Pt, 24·5%].

The *nitrosoamine*, prepared by the addition of sodium nitrite to

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* It is somewhat remarkable that azobenzene is reduced by sodium and boiling ethyl alcohol only with great difficulty.

a solution of the base in cold hydrochloric acid, crystallises from ether in fine, pale yellow needles, m. p. 44—48° (Found: N, 12·8. $C_{12}H_{18}O_2N_2$ requires N, 12·6%).

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