CCXLVIII.—*The Condensation of α -Keto- β -anilino- $\alpha\beta$ -diphenylethane and its Homologues with Phenylcarbimide and with Phenylthiocarbimide.*

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WHEN α -keto- β -anilino- $\alpha\beta$ -diphenylethane (I) and phenylcarbimide are heated together, a compound results which has the formula $C_{27}H_{22}O_2N_2$, that is, direct addition of the two molecules has taken place :

In α -keto- β -anilino- $\alpha\beta$ -diphenylethane there are two possible points of attack for the phenylcarbimide. In the first place, the secondary amine grouping might be attacked, and the resulting compound would be desyl-*s*-diphenylcarbamide (II). That secondary amines do react with phenylcarbimide has been shown by Gebhardt in the case of diethylamine (*Ber.*, 1884, **17**, 3039) and methyl- and ethyl-aniline (*Ber.*, 1884, **17**, 2093).

In many reactions α -keto- β -anilino- $\alpha\beta$ -diphenylethane and its derivatives are capable of reacting in the enolic form (III). Examples of this behaviour are furnished by its ready conversion into diphenylindole (Japp and Murray, *Ber.*, 1893, **26**, 2638; Lachewicz, *Monatsh.*, 1894, **15**, 402), by the conversion of the acyl derivatives into glyoxalines (Everest and McCombie, *Trans.*, 1911, **99**, 1746), and the condensation with carbonyl chloride and thionyl chloride (McCombie and Parkes, this vol., p. 1991). If these reactions are taken into consideration, it is possible that phenylcarbimide might react with the hydroxyl group of the enolic form, resulting in the compound having the constitution IV.

On boiling the compound $C_{27}H_{22}O_2N_2$ with alcoholic hydrogen chloride, a molecule of water was eliminated, and a substance possessing the formula $C_{27}H_{20}ON_2$ was obtained. This substance was found to be very stable towards acids and alkalis, no salt with hydrochloric acid could be obtained (although a picrate could be prepared); and phosphorus pentachloride was without action on it. Starting with compounds represented by formulæ III and IV, water could be eliminated, resulting in compounds of formula V and VI respectively. The great stability of the compound argues against formula VI:

A further argument against this formula is furnished by a study of the reaction between α -keto- β -anilino- $\alpha\beta$ -diphenylethane and phenylthiocarbimide. In this case, after treating the reaction mixture with alcoholic hydrogen chloride, a compound free from oxygen, and having the formula $C_{27}H_{20}N_2S$ was obtained. The two possible formulæ for the intermediate product in this case are VII and VIII:

From a substance with the formula VIII, since the only oxygen atom is directly attached to the two carbon atoms, it would be impossible to eliminate the elements of water. From this it follows that the products formed by the action of phenyl-thiocarb-

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imide and -carbimide respectively on α -keto- β -anilino- $\alpha\beta$ -diphenylethane when treated with alcoholic hydrogen chloride are 1:3:4:5 - tetraphenyl-2:3-dihydro-2-glyoxalthione* (IX) and 1:3:4:5-tetraphenyl-2:3-dihydro-2-glyoxalone (V):

The salts formed by the glyoxalones with picric acid gave some unexpected results. The picrates could be divided into two classes. Those derived from the tetraphenyl-, the triphenyl-*p*-tolyl-, and the triphenyl- β -naphthyl-glyoxalones were all red, and consisted of two molecules of the glyoxalone united with one molecule of picric acid. On the other hand, the picrates derived from the triphenyl-*m*-tolyl- and the triphenyl-*o*-tolyl-glyoxalones were yellow, and consisted of the glyoxalone and picric acid in equimolecular proportions.

EXPERIMENTAL.

The Action of Phenylcarbimide on α -Keto- β -anilino- $\alpha\beta$ -diphenylethane.

Ten grams of α -keto- β -anilino- $\alpha\beta$ -diphenylethane were heated on a water-bath with 4.6 grams of phenylcarbimide until a colourless, vitreous mass was formed. The excess of phenyl carbimide was removed by warming for a short time with a small quantity of methyl alcohol, and the white product, recrystallised from methyl alcohol, separated in white needles melting at 116—117°. It contained methyl alcohol of crystallisation. The yield was theoretical:

0.1963 gave 0.5558 CO₂ and 0.1049 H₂O. C=77.22; H=5.94.

0.2704 „ 15.3 c.c. N₂ at 12° and 747 mm. N=6.57.

C₂₇H₂₂O₂N₂·MeOH requires C=76.70; H=5.94; N=6.39 per cent.

The product was sparingly soluble in cold alcohol, practically insoluble in cold benzene, but very soluble in hot benzene, from which it crystallised in needles melting at 124—125°, and contained benzene of crystallisation:

0.2017 gave 0.6013 CO₂ and 0.1090 H₂O. C=81.30; H=6.00.

C₂₇H₂₂O₂N₂·C₆H₆ requires C=81.65; H=5.78 per cent.

1:3:4:5-Tetraphenyl-2:3-dihydro-2-glyoxalone, C₂₇H₂₀ON₂.

The product obtained from the action of phenylcarbimide on α -keto- β -anilino- $\alpha\beta$ -diphenylethane, when boiled for several hours

* The termination "thione" appears to be a suitable one to designate a glyoxalone in which the CO-group is replaced by the CS-group.

with hydrochloric acid in alcohol, gave a substance which, after crystallisation from alcohol or benzene, separated in white needles melting at 204°. The compound is sparingly soluble in cold alcohol, more so in cold benzene, and very soluble in hot benzene or acetic acid:

0.2063 gave 0.6336 CO₂ and 0.0972 H₂O. C=83.76; H=5.24.

0.2154 „ 13.7 c.c. N₂ at 15° and 746.2 mm. N=7.27.

C₂₇H₂₀ON₂ requires C=83.50; H=5.16; N=7.22 per cent.

The glyoxalone is a very stable compound; its basicity is so slight that no hydrochloride could be prepared in either acetic acid or alcoholic solution. A picrate, however, was obtained. When the glyoxalone was heated in a sealed tube with aniline or phenylhydrazine, no condensation product could be isolated. Phosphorus pentachloride in benzene solution was without action on the glyoxalone.

The *picrate* was prepared by adding excess of picric acid to a concentrated solution of the glyoxalone in boiling acetic acid. The solution, on cooling, deposited dark red needles, which, after recrystallisation from absolute alcohol or acetic acid, melted at 171°:

0.1663 gave 0.4348 CO₂ and 0.0643 H₂O. C=71.30; H=4.30.

2C₂₇H₂₀ON₂.C₆H₃O₇N₃ requires C=71.65; H=4.29 per cent.

The *picrate* was readily decomposed by boiling with water or alkali, with regeneration of the glyoxalone. From the analysis it is evident that the salt contains two molecules of the base united with one molecule of picric acid.

3:4:5-Triphenyl-1-*o*-tolyl-2:3-dihydro-2-glyoxalone.

This compound, when crystallised from alcohol, melted at 193°:

0.1964 gave 0.6020 CO₂ and 0.0978 H₂O. C=83.6; H=5.52.

C₂₈H₂₂ON₂ requires C=83.57; H=5.47 per cent.

The *picrate* crystallises from acetic acid in yellow prisms melting at 169°:

0.2018 gave 0.4764 CO₂ and 0.0732 H₂O. C=64.40; H=4.02.

C₂₈H₂₂ON₂.C₆H₃O₇N₃ requires C=64.67; H=3.96 per cent.

Analysis shows that this salt consists of molecular proportions of the glyoxalone and picric acid.

3:4:5-Triphenyl-1-*m*-tolyl-2:3-dihydro-2-glyoxalone.

This compound crystallises from methyl alcohol or a mixture of benzene and light petroleum in slender needles melting at 185°:

0.1769 gave 0.5427 CO₂ and 0.0880 H₂O. C=83.67; H=5.53.

C₂₈H₂₂ON₂ requires C=83.57; H=5.47 per cent.

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The *picrate* crystallises from absolute alcohol in yellow prisms melting at 172° :

0.2076 gave 0.4913 CO_2 and 0.0744 H_2O . $\text{C}=64.6$; $\text{H}=3.98$.

$\text{C}_{28}\text{H}_{22}\text{ON}_2, \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ requires $\text{C}=64.67$; $\text{H}=3.96$ per cent.

Analysis shows that this salt consists of molecular proportions of the glyoxalone and picric acid.

3:4:5-Triphenyl-1-p-tolyl-2:3-dihydro-2-glyoxalone.

Five grams of α -keto- β -p-toluidino- $\alpha\beta$ -diphenylethane were heated with 2 grams of phenylcarbimide on a water-bath for one and a-half hours. The product was then boiled for several hours with hydrogen chloride in alcoholic solution; the crystals were collected and recrystallised from absolute alcohol, when the substance separated in white needles melting at 206° . It is only sparingly soluble in cold solvents with the exception of acetic acid:

0.1941 gave 0.5943 CO_2 and 0.0965 H_2O . $\text{C}=83.50$; $\text{H}=5.53$.

$\text{C}_{28}\text{H}_{22}\text{ON}_2$ requires $\text{C}=83.57$; $\text{H}=5.47$ per cent.

The *picrate* crystallises from absolute alcohol in dark red needles melting at 188° :

0.1610 gave 0.4256 CO_2 and 0.0652 H_2O ; $\text{C}=72.1$; $\text{H}=4.5$.

$2\text{C}_{28}\text{H}_{22}\text{ON}_2, \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ requires $\text{C}=72.04$; $\text{H}=4.55$ per cent.

From the analysis it is seen that this *picrate* contains two molecules of the glyoxalone united with one molecule of picric acid.

3:4:5-Triphenyl-1- β -naphthyl-2:3-dihydro-2-glyoxalone.

This substance was prepared in the same way as the other compounds, and when recrystallised from methyl alcohol it gave masses of small, white needles, melting at 182 — 183° .

It is readily soluble in acetic acid, benzene, hot alcohol, or light petroleum, but less so in the cold solvents. It is sparingly soluble in ether, and is stable towards alkalis and acids:

0.1982 gave 0.6159 CO_2 and 0.0890 H_2O . $\text{C}=84.76$; $\text{H}=4.99$.

$\text{C}_{31}\text{H}_{22}\text{ON}_2$ requires $\text{C}=84.91$; $\text{H}=5.02$ per cent.

The *picrate* was obtained in acetic acid solution, and separated from absolute alcohol in pale red crystals melting at 201° :

0.2005 gave 0.5387 CO_2 and 0.0821 H_2O . $\text{C}=73.30$; $\text{H}=4.55$.

$2\text{C}_{31}\text{H}_{22}\text{ON}_2, \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ requires $\text{C}=73.85$; $\text{H}=4.25$ per cent.

Analysis shows that the glyoxalone and picric acid are present in the proportion of 2:1

Preparation of 1:3:4:5-Tetraphenyl-2:3-dihydro-2-glyoxalithione and its Homologues.

These compounds were prepared in a manner similar to that employed in the preparation of the corresponding glyoxalones. The anilino-derivative and the phenylthiocarbimide were heated together for a few hours in an air-bath, or for a longer time on a water-bath. Water was then eliminated from the compound by boiling with alcoholic hydrogen chloride.

The glyoxalithiones thus prepared are only sparingly soluble in methyl or ethyl alcohols, more readily so in amyl alcohol or acetic acid, and very soluble in acetone or benzene.

1:3:4:5-Tetraphenyl-2:3-dihydro-2-glyoxalithione, C₂₇H₂₀N₂S.

This substance crystallises from glacial acetic acid in slender, white needles, melting at 249—250°:

0·2068 gave 0·6059 CO₂ and 0·0936 H₂O. C=79·90; H=5·03.

0·2002 „ 11·95 c.c. N₂ at 14·2° and 752·8 mm. N=6·91.

0·3716 „ 0·2166 BaSO₄. S=8·01.

C₂₇H₂₀N₂S requires C=80·19; H=4·96; N=6·93; S=7·92 per cent.

3:4:5-Triphenyl-1-o-tolyl-2:3-dihydro-2-glyoxalithione.

When recrystallised from amyl alcohol this compound melted at 240°:

0·2046 gave 0·6018 CO₂ and 0·0952 H₂O. C=80·22; H=5·17.

C₂₈H₂₂N₂S requires C=80·38; H=5·26 per cent.

3:4:5-Triphenyl-1-m-tolyl-2:3-dihydro-2-glyoxalithione.

When recrystallised from absolute alcohol this substance separated in slender, white needles, melting at 189°:

0·1987 gave 0·5851 CO₂ and 0·0963 H₂O. C=80·30; H=5·39.

C₂₈H₂₂N₂S requires C=80·38; H=5·26 per cent.

3:4:5-Triphenyl-1-p-tolyl-2:3-dihydro-2-glyoxalithione.

This substance was obtained in slender needles melting at 234°, after recrystallisation from glacial acetic acid or amyl alcohol:

0·2041 gave 0·6004 CO₂ and 0·0992 H₂O. C=80·24; H=5·40.

C₂₈H₂₂N₂S requires C=80·38; H=5·26 per cent.

α-Keto-β-2-naphthylamino-αβ-diphenylethane,
 $\text{COPh} \cdot \text{CHPh} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$.

This compound has been prepared by Bischla and Fireman (*Ber.*, 1893, **26**, 1339) by the decomposition of β -bromo- α -keto- $\alpha\beta$ -diphenylethane with β -naphthylamine in alcoholic solution, and also by Voigt (*J. pr. Chem.*, 1886, [ii], **34**, 22) from benzil and β -naphthylamine at 215° .

We have prepared it from benzoin in the usual manner, by heating the two substances together in an air-bath at 150° for three and a-half hours. The product was crystallised from amyl alcohol, when it melted at 131 — 132° .

The hydrochloride was obtained in slender crystals, melting and decomposing at 200° .

3:4:5-Triphenyl-1-β-naphthyl-2:3-dihydro-2-glyoxalthane.

This compound was more difficult to prepare owing to charring taking place. After repeated recrystallisations from amyl alcohol, crystals melting at 219° were obtained. This glyoxalthane is readily soluble in acetone or benzene, and sparingly so in cold methyl or ethyl alcohols:

0.2015 gave 0.6035 CO_2 and 0.0910 H_2O . $\text{C}=81.70$; $\text{H}=5.01$.

$\text{C}_{31}\text{H}_{22}\text{N}_2\text{S}$ requires $\text{C}=81.91$; $\text{H}=4.85$ per cent.

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