CXLVI.—*The Constitution of the Aldol Bases.*

By MURIEL GWENDOLEN EDWARDS, RALPH EDDOWES GARROD,
and HUMPHREY OWEN JONES.

THE isomeric compounds, called for brevity "aldol bases," $C_{12}H_{17}ON$, obtained by von Miller and Plöchl (*Ber.*, 1896, **29**, 1462) by the interaction of *m*-4-xylidine and acetaldehyde in dilute hydrochloric acid solution, were given the structural formula

and the isomerism was attributed to a different spatial arrangement of the three groups attached to the tervalent nitrogen atom.

This case of isomerism was studied by one of us and E. J. White (*Trans.*, 1910, **97**, 633), and it was shown that the explanation suggested by von Miller and Plöchl was untenable. The isomerides

are not interconvertible under the influence of heat or of organic solvents as stated by these authors, but each is transformed into a mixture of the two by the action of acids. The α -compound (m. p. 103—104°) and the β -compound (m. p. 127—128°) gave the same monobenzoyl derivative by the Schotten-Baumann method, the same derivative with hydroxylamine hydrochloride, and the same condensation product, $C_{20}H_{28}N_2$, bimolecular ethyldenexylidene, or double Schiff's base, with *m*-4-xylidine. The hydrochlorides of the α - and β -bases were, however, different, and so, apparently, were the products obtained by the action of nitrous acid on the bases, but only the derivative of the β -base was obtained crystalline and analysed.

The absorption spectra of the bases was almost identical (Purvis, *Trans.*, 1910, **97**, 644).

It was then suggested tentatively that the bases were structurally different, and might be represented by the formulæ:

The hydroxytrimethyleneimine ring in the latter compound would probably be unstable (compare Howard and Marckwald, *Ber.*, 1899, **32**, 2031), especially in the presence of acids, and so the formation of a number of identical derivatives would be explained.

The alternative of representing the bases as *cis*- and *trans*-forms of a hydroxytetrahydroquinoline derivative was considered and rejected, mainly because it was considered improbable that the tetrahydroquinoline ring would be so readily formed and would so easily undergo fission.

In the same paper it was shown that two similar isomeric compounds could be obtained from *p*-toluidine and from ψ -cumidine.

The study of these compounds has now been considerably extended, and a thorough examination of the two *p*-toluidine aldol bases has been made; the one isomeride obtainable from 3-bromo-*p*-toluidine, and the more easily obtainable of the two ψ -cumidine aldol bases have also been examined. In all these cases the problem is rendered more difficult owing to the ease with which the aldol bases are converted into a quinoline and a tetrahydroquinoline derivative under the influence of acids or of heat.

The double Schiff's bases, corresponding with bimolecular ethyldenexylidene, from the above amines have also been prepared and their derivatives studied.

Although mesidine and 5-bromo-*m*-4-xylidine have been treated with acetaldehyde under various conditions, no aldol base or double Schiff's base has been obtained from either of these compounds.

The only fact that seemed inconsistent with the view previously suggested to account for the isomerism of the aldol bases was the apparent existence of two different nitroso-derivatives of the isomeric compounds obtained from *m*-4-xylylidine. The whole problem was altered and the clue to its solution obtained when it was clearly established that the two isomeric aldol bases obtained from *p*-toluidine gave two different monobenzoyl derivatives, both insoluble in acids, whereas, as stated above, the α - and β -aldol bases from *m*-4-xylylidine had furnished the same derivative.

It was then found that the products of the action of nitrous acid on the α - and β -aldol bases of *m*-4-xylylidine could be obtained crystalline, that both were true nitroso-derivatives, $C_{12}H_{16}ON \cdot NO$, and that each could be benzoylated and acetylated. The isomeric *p*-toluidine aldol bases also gave nitroso-compounds, which could be benzoylated and acetylated to give isomeric acyl-nitroso-compounds.

The original α - and β -aldol bases from these acyl nitroso-compounds, when treated with sodium and alcohol, were regenerated. These observations show that each of the isomeric aldol bases is probably a secondary base containing a hydroxyl group.

This conclusion was supported by the fact that the α - and β -xylylidine aldol bases gave a dibenzoyl derivative when allowed to remain with benzoyl chloride in pyridine solution from twenty-four to forty-eight hours, and, further, the β -isomeride in the case of *p*-toluidine and xylylidine gave a crystalline diacetyl derivative. It is curious, however, that no dibenzoyl compound could be obtained from either of the *p*-toluidine aldol bases.

A consideration of these facts leads to the conclusion that these isomeric bases must be represented as stereoisomeric (*cis* and *trans*) forms of hydroxytetrahydroquinoline derivatives; thus:

in the case of the *p*-toluidine compounds.

This view accounts for all the facts which we have observed, the most important of which are summarised above, and also for the great similarity which these compounds show in their absorption spectra and physical properties, such as refractive power and viscosity of solutions, which have also been examined and will be described later. On this view, too, the formation of aldol bases from mesidine and 5-bromo-*m*-4-xylylidine is impossible.

The hydroxytetrahydroquinoline ring must be very unstable and capable of fission with great ease, especially under the influence of acids, so that the α - and β -bases give the same oxime.

It has been shown that the monobenzoyl derivative (m. p. 150—151°) obtained from both the xylidine aldol bases is really a derivative of the β -aldol base, because on treatment with benzoyl chloride in pyridine solution it is converted into the dibenzoyl derivative of the β -aldol base. It would therefore appear that the α -aldol base or its benzoyl derivative is transformed into the β -compound under the influence of benzoyl chloride or acid in the Schotten-Baumann method of benzoylation.

No compound of the type of these hydroxytetrahydroquinoline derivatives is known, and hitherto we have not been able to reduce the corresponding hydroxyquinoline derivative, 4-hydroxy-2:6-dimethylquinoline, and 4-hydroxy-2:6:8-trimethylquinoline (Conrad and Limpach, *Ber.*, 1888, **21**, 525) to the corresponding hydroxytetrahydroquinoline; alkaline reducing agents have no action on these compounds, whilst acid reducing agents, if they produced the hydroxytetrahydroquinoline, would naturally cause this to undergo transformation into quinoline and tetrahydroquinoline. We have been able to show that tin and hydrochloric acid convert the above hydroxyquinoline derivatives into the corresponding tetrahydroquinoline derivatives, a change which is best explained by the intermediate formation of a hydroxytetrahydroquinoline or aldol base.

The double Schiff's bases, $C_{20}H_{26}N_2$ in the case of xylidine, might be constituted similarly to the aldol bases, that is:

or they might be represented as

as suggested by von Miller and Plöchl.

A study of their properties supports the second mode of representation, as they give monoacetyl, monobenzoyl, and mononitroso-derivatives only, but it follows that the tetrahydroquinoline ring must be broken by mere heating with xylidine in the case of the α - and β -xylidine aldol bases, which are thus converted into the double Schiff's base. This change does not take place in the case of the *p*-toluidine aldol bases.

EXPERIMENTAL.

p-Toluidine Derivatives. α - and β -Aldol Bases, $C_{11}H_{15}ON$.

A mixture of the isomeric bases was prepared by the action of acetaldehyde on *p*-toluidine (Trans., 1910, **97**, 643) in a manner analogous to that used in the case of the corresponding xylylidine compounds. In this case, however, a small quantity of a brown, tarry material was always produced, and was difficult to remove entirely from the α -compound.

The separation of the α - and β -isomerides was effected by shaking the mixture with alcohol (40 grams of mixture to 200 c.c. of alcohol), when the β -base melting at 164–167° (when heated rapidly, 165–169°) was obtained practically pure from the undissolved solid, and was recrystallised from alcohol, from which it separated in lustrous plates.

The α -base was isolated by evaporation of the alcoholic solution. The coloured product was purified by repeated recrystallisation from benzene or petroleum (b. p. 90–100°), and separated in soft, brittle plates, melting at 108–110°.

The wide range of melting in the case of these two bases is due to the fact that, even at the lower temperature, the quinoline transformation has already set in, and is rapid at the melting point of the β -base.

Either isomeride, when treated with sodium and alcohol, was recovered unchanged.

Derivatives of p-Toluidine Aldol Bases.

Action of Hydrogen Chloride.—On passing dry hydrogen chloride into a solution of the β -base in ether or benzene, the hydrochloride separated as a white powder, melting at 126–127°.

Under similar conditions, the α -hydrochloride separated as a white powder, but was extremely deliquescent, and when left exposed to the air for some hours, at first became viscid, and then appeared to become dry, when it was found to have been converted into the β -hydrochloride.

Oxime.—By the action of hydroxylamine hydrochloride in alcohol and water, the same oxime was obtained from both α - and β -aldol base, the yield being very poor. The substance was recrystallised from alcohol, and melted at 132–134°:

0.1372 gave 0.3459 CO_2 and 0.1061 H_2O . $C = 68.7$; $H = 8.6$.

$C_{11}H_{16}ON_2$ requires $C = 68.8$; $H = 8.34$ per cent.

*Acyl Derivatives of p-Toluidine Aldol Bases.**Action of Acetyl Chloride.*

β-Compound.—Acetylation was conducted in pyridine solution, the product separating from rectified spirit in very well defined, short, lustrous prisms or diamond-shaped plates, melting at 117–119°, which were only sparingly soluble in light petroleum:

0.1965 gave 0.4930 CO₂ and 0.1275 H₂O. C=68.6; H=7.2.

0.1235 „ 5.7 c.c. N₂ at 14° and 754 mm. N=5.5.

C₁₅H₁₉O₃N requires C=69.0; H=7.28; N=5.36 per cent.

The compound is therefore a diacetyl derivative.

The *α-derivative*, similarly prepared, was a gum, and could not be obtained crystalline.

Benzoyl Compounds.—The benzoyl derivatives of the *α*- and *β*-bases were prepared by the Schotten-Baumann process, and were recrystallised from benzene. The *β-compound* was obtained in short prisms or stout, rectangular plates, tending to form stellate aggregates, and melting at 170–172°:

0.2143 gave 0.5985 CO₂ and 0.1322 H₂O. C=76.3; H=6.85.

C₁₈H₁₉O₂N requires C=76.8; H=6.76 per cent.

The *α-compound* separated from benzene in long needles, melting at 145–146°, which tended to be quite thin and to form a felted mass:

0.2081 gave 9.3 c.c. N₂ at 17° and 722 mm. N=5.03.

C₁₈H₁₉O₂N requires N=4.98 per cent.

This is therefore a monobenzoyl derivative.

Both *α*- and *β*-aldol bases gave the same monobenzoyl derivatives in pyridine solution as by the Schotten-Baumann process, in striking contrast to the corresponding xylidine compounds.

Action of Nitrous Acid.

β-p-Toluidine Aldol Base.—1.77 Grams of the base dissolved in 30 c.c. of *N*-sulphuric acid were cooled and quickly poured into a solution of 2.5 grams of sodium nitrite in 300 c.c. of cold water. An oil separated, which crystallised on keeping, and was purified by crystallisation from alcohol, or, better, from benzene, when it formed long, yellow prisms, melting at 108–110°:

0.2015 gave 0.4710 CO₂ and 0.1290 H₂O. C=63.8; H=7.11.

C₁₁H₁₄O₂N₂ requires C=64.1; H=6.8 per cent.

The same product was obtained when one molecular proportion of sodium nitrite, dissolved in water, was poured into the aldol base solution. In the case of the *α*-toluidine aldol base, either method

only gave a viscid substance, which did not crystallise. The pure β -compound and the oil obtained from the α -base gave Liebermann's nitroso-reaction, and were insoluble in acids. They would therefore appear to be nitroso-compounds of secondary amines, and on reduction the original aldol bases were recovered.

Benzoylation of Nitroso-derivatives.

The nitroso-compounds obtained from the α - and β -aldol bases were benzoylated by the Schotten-Baumann method.

Benzoyl-nitroso- β -aldol Base.—The compound separated from benzene in yellow plates mixed with a few needles, melting at 124 — 125° , and having a duller brown tinge than the original nitroso-derivative:

0.2023 gave 0.5180 CO_2 and 0.1062 H_2O . $\text{C}=69.8$; $\text{H}=5.8$.

$\text{C}_{18}\text{H}_{18}\text{O}_3\text{N}_2$ requires $\text{C}=69.7$; $\text{H}=5.81$; $\text{N}=9.04$ per cent.

The compound was therefore a benzoyl-nitroso-derivative. It gave Liebermann's nitroso-reaction. On reduction with sodium and alcohol, ammonia was evolved, and the β -*p*-toluidine aldol base obtained, so that removal of the nitroso- and benzoyl groups occurred simultaneously.

Benzoyl-nitroso- α -aldol Base.—The compound which was prepared from the viscid α -nitroso-compound separated from alcohol in yellow needles, melting at 130 — 132° , and brighter in colour than the corresponding β -compound. When mixed with the latter, the mixture melted at 107 — 110° :

0.2024 gave 0.5147 CO_2 and 0.1070 H_2O . $\text{C}=69.4$; $\text{H}=5.8$.

0.2825 „ 23.2 c.c. N_2 at 19° and 740 mm. $\text{N}=9.4$.

This is therefore a benzoyl-nitroso-compound isomeric with that obtained from the β -aldol base, and, like it, giving Liebermann's test.

On reduction with sodium and alcohol, ammonia was evolved, and the α -*p*-toluidine aldol base obtained, contaminated with a trace of the β -base, that is, in this case also the nitroso- and benzoyl groups were removed simultaneously. No change was produced by the action of the aluminium-mercury couple and alcoholic sodium hydroxide, or by hydrogen and colloidal palladium.

Action of Acetyl Chloride on the Nitroso-compounds.

The nitroso-compounds of the α - and β -*p*-toluidine aldol bases do not give such well-characterised acetyl compounds as the corresponding xylidine derivatives when treated with acetyl chloride in pyridine solution, but the β -compound was obtained crystalline in yellow prisms, which were somewhat difficult to recrystallise, and

tended to become viscid, so that they could not be obtained pure. They melted at 68—69°:

0.2691 gave 26.0 c.c. N_2 at 16° and 751 mm. $N=11.3$.

$C_{13}H_{16}O_3N_2$ requires $N=11.3$ per cent.

Double Schiff's Base of p-Toluidine.

This compound was prepared by neutralising a mixture of toluidine and acetaldehyde in equimolecular proportions in hydrochloric acid after allowing it to remain for one to two hours. The product was sparingly soluble in light petroleum, and soluble in alcohol, thereby differing from the corresponding xyloidine compound. It separates from alcohol in well-defined, lustrous prisms, melting at 114—116°:

0.2010 gave 0.5970 CO_2 and 0.1495 H_2O . $C=81.0$; $H=8.27$.

0.3918 „, 35.2 c.c. N_2 at 13° and 753 mm. $N=10.7$.

$C_{18}H_{22}N_2$ requires $C=81.2$; $H=8.27$; $N=10.5$ per cent.

From its method of production and the fact that none can be obtained after the reaction mixture has remained for several hours, it would appear that the formation of this compound precedes the formation of the isomeric aldol base.

The acetyl compound formed in pyridine solution could not be obtained crystalline.

The *nitroso*-derivative was produced by pouring a solution of the base in dilute sulphuric acid into excess of dilute sodium nitrite in the cold. The yellow precipitate was collected and dissolved in alcohol, from which it separated in brownish-yellow plates, melting at 135.7°:

0.2135 gave 26.0 c.c. N_2 at 15° and 764 mm. $N=14.6$.

$C_{18}H_{21}ON_3$ requires $N=14.2$ per cent.

The compound is therefore a mononitroso-derivative.

m-4-Xyloidine Aldol Bases and Derivatives.

The preparation and separation of these isomeric bases has been already described (*Trans.*, 1910, **97**, 635), together with that of the derived oxime, benzoyl compound, and products of the action of hydrogen chloride.

A preliminary mechanical separation was generally necessary in the preparation of the α - and β -aldol bases, although occasionally by fractional crystallisation a crop of practically pure crystals of α -compound (m. p. 103—104°) was obtained. The less soluble β -compound melting at 127—128° is quite easily obtained in a state of purity.

Acetyl Derivatives of m-4-Xylidine Aldol Bases.

Acetylation of the β -aldol base was effected in pyridine, the product being difficult to crystallise. It separated from ether, and very well from petroleum, in rectangular prisms and hexagonal plates melting at 94—95°:

0.2200 gave 0.5625 CO_2 and 0.1505 H_2O . $\text{C}=69.7$; $\text{H}=7.6$.

0.3575 „ 16.4 c.c. N_2 at 18° and 754 mm. $\text{N}=5.38$.

$\text{C}_{16}\text{H}_{21}\text{O}_3\text{N}$ requires $\text{C}=69.8$; $\text{H}=7.64$; $\text{N}=5.1$ per cent.

The derivative was therefore a diacetyl compound. The acetyl derivative of the α -aldol base was obtained as a gum, which crystallised, only after long keeping, in thin plates melting at 70—71°.

Benzoyl Compounds of α - and β -Xylidine Aldol Bases.

By the Schotten-Baumann method the same monobenzoyl compound, melting at 150—151°, is obtained from both isomerides as previously mentioned (Jones and White, *Trans.*, 1910, **97**, 641). In order to see if the same result was obtained under different conditions, the mixture of the α - or β -aldol base with benzoyl chloride in pyridine solution was allowed to remain for twenty-four or forty-eight hours.

α -Xylidine-aldol base thus gave a product which separated from alcohol in well-defined, lustrous prisms, melting at 143—144°. A mixture of this with the monobenzoyl compound melted at 122—126°:

0.1935 gave 0.5550 CO_2 and 0.1075 H_2O . $\text{C}=78.2$; $\text{H}=6.17$.

0.3190 „ 10.0 c.c. N_2 at 21° and 743 mm. $\text{N}=3.56$.

$\text{C}_{26}\text{H}_{25}\text{O}_3\text{N}$ requires $\text{C}=78.2$; $\text{H}=6.27$; $\text{N}=3.51$ per cent.

The compound is therefore a dibenzoyl derivative of the α -aldol base, in which both the secondary nitrogen and the hydroxyl group have reacted with benzoyl chloride.

β -Xylidine aldol base, when treated in the same way, gave a product which separated from alcohol in flat prisms and plates melting at 145—146°.

A mixture of this with the monobenzoyl compound melted at 128—134°, and a mixture with the compound obtained from the α -base melted below 125°:

0.4847 gave 15.0 c.c. N_2 at 19° and 739 mm. $\text{N}=3.53$.

The compound is therefore a dibenzoyl derivative different from the dibenzoyl derivative of the α -base.

On treating the monobenzoyl derivative (m. p. 150—151°) with benzoyl chloride in pyridine solution, a compound identical with the dibenzoyl derivative of the β -aldol base was obtained, so that

the compound produced by the Schotten-Baumann method is to be regarded as a derivative of the β -aldol base.

Action of Nitrous Acid.—The product from the β -base has been already described (*loc. cit.*, p. 642), and has since been obtained in pale yellow, lustrous octahedra, melting at 117° .

Xylidine α -Aldol Base and Nitrous Acid.

To 1.91 grams of the α -base dissolved in 20 c.c. of *N*-sulphuric acid were added gradually 0.7 gram (1 molecular proportion) of sodium nitrite dissolved in 150 c.c. of water. The oily precipitate which formed was extracted with benzene, from which solvent long, slender, yellow prisms separated, melting at 80 – 81° :

0.1485 gave 0.3575 CO_2 and 0.0970 H_2O . $\text{C}=65.6$; $\text{H}=7.26$.

0.1759 „ 18.7 c.c. N_2 at 18° and 741 mm. $\text{N}=12.3$.

$\text{C}_{12}\text{H}_{16}\text{O}_2\text{N}_2$ requires $\text{C}=65.5$; $\text{H}=7.27$; $\text{N}=12.7$ per cent.

so that the compound is a mononitroso-derivative.

The reduction of either the α - or β -nitroso-compound with sodium and alcohol regenerated the corresponding aldol base.

When 0.6 gram of the α -aldol base dissolved in 10 c.c. of *N*-sulphuric acid was poured into a solution of 0.8 gram of sodium nitrite dissolved in 50 c.c. of cold water, and extracted with petroleum, a yellow, crystalline solid separated, melting at 92 – 98° , but this could not be recrystallised. On repeating the process with larger quantities, prisms separated, melting at 97 – 103° . A mixture of these with the β -nitroso-derivative melted at 80° .

Analyses were made of three different specimens after drying in a vacuum, and very concordant results were obtained, of which one may be quoted as typical:

0.2380 gave 0.5030 CO_2 and 0.1345 H_2O . $\text{C}=57.7$; $\text{H}=6.3$.

0.1867 „ 26.45 c.c. N_2 at 18° and 766 mm. $\text{N}=16.8$.

$\text{C}_{12}\text{H}_{16}\text{O}_3\text{N}_3$ requires $\text{C}=57.6$; $\text{H}=6.4$; $\text{N}=16.8$ per cent.

and it was therefore concluded that this compound was an additive compound of the NO -group and a nitroso-derivative, or possibly it is a dinitroso-compound. No evidence is available for deciding the position of the second nitroso-group.

Action of Benzoyl Chloride on Nitroso- β -xylidine Aldol Base.

As the Schotten-Baumann method tried in two experiments was not satisfactory, the action of benzoyl chloride in pyridine was investigated.

To 1.91 grams of the nitroso-compound dissolved in 20 c.c. of pyridine were added 1.4 grams of benzoyl chloride, and the whole

was allowed to remain for four hours, after which it was poured into dilute sulphuric acid and extracted with ether. The product separated from rectified spirit in almost colourless, rectangular prisms, melting at 110—111°, and giving a well-marked Liebermann reaction :

0.2018 gave 0.5205 CO_2 and 0.1140 H_2O . $\text{C}=70.3$; $\text{H}=6.28$.

$\text{C}_{10}\text{H}_{20}\text{O}_3\text{N}_2$ requires $\text{C}=70.3$; $\text{H}=6.17$ per cent.

The compound is therefore a benzoyl-nitroso-derivative.

On heating the above substance a gas is evolved, slowly at 160° and rapidly at 170°.

Benzoyl chloride appeared to have no action on the nitroso-derivative of the α -aldol base in presence of sodium hydroxide or in pyridine solution after a few hours. On allowing the mixture in pyridine to remain for two days a viscid oil was obtained, which only showed signs of crystallising after keeping for a long time.

Action of Acetyl Chloride on Nitroso- β -xylylidine Aldol Base.

The product obtained in pyridine separated from alcohol in pale yellow, rectangular prisms, melting at 110—111°, giving Liebermann's reaction, and remaining unchanged when boiled with sodium hydroxide solution :

0.2357 gave 0.5560 CO_2 and 0.1500 H_2O . $\text{C}=64.3$; $\text{H}=7.07$.

0.3012 „ 28.1 c.c. N_2 at 15° and 735.5 mm. $\text{N}=10.7$.

$\text{C}_{14}\text{H}_{18}\text{O}_3\text{N}_2$ requires $\text{C}=64.1$; $\text{H}=6.87$; $\text{N}=10.7$ per cent.

Acetyl-nitroso-derivative of the α -Aldol Base.

In pyridine a gum was obtained which crystallised on keeping, and separated from alcohol in pale yellow, rectangular prisms, melting at 87—89°:

0.2865 gave 27.1 c.c. N_2 at 17° and 755.5 mm. $\text{N}=11.0$.

$\text{C}_{14}\text{H}_{18}\text{O}_3\text{N}_2$ requires $\text{N}=10.7$ per cent.

The nitroso-derivatives of the α - and β -aldol bases therefore react with acetyl chloride to yield different acetyl-nitroso-compounds.

Derivatives of Double Schiff's Base of m-4-Xylylidine.

The *hydrochloride* was precipitated in colourless needles by passing dry hydrogen chloride into a solution of the base in light petroleum. On keeping, it became coloured, and was found to change into a mixture of xylylidine with quinoline derivatives :

0.2030 gave 0.1566 AgCl . $\text{Cl}=19.1$.

$\text{C}_{20}\text{H}_{26}\text{N}_2 \cdot 2\text{HCl}$ requires $\text{Cl}=19.3$ per cent.

The *compound* with trinitrobenzene separated from alcohol in black, lustrous prisms, melting at 132° :

0.2752 gave 0.5380 CO_2 and 0.1115 H_2O . $\text{C}=53.3$; $\text{H}=4.50$.

$\text{C}_{20}\text{H}_{26}\text{N}_2 \cdot 2\text{C}_6\text{H}_3\text{O}_6\text{N}_3$ requires $\text{C}=53.3$; $\text{H}=4.44$ per cent.

The *acetyl* derivative was prepared in pyridine solution, and separated from alcohol in fine rhombs melting at $144\text{--}145^{\circ}$:

0.1920 gave 0.5515 CO_2 and 0.1434 H_2O . $\text{C}=78.4$; $\text{H}=8.30$.

$\text{C}_{22}\text{H}_{28}\text{ON}_2$ requires $\text{C}=78.6$; $\text{H}=8.33$ per cent.

The compound is therefore a monoacetyl derivative.

The *benzoyl* derivative obtained by the Schotten-Baumann method separated from alcohol in lustrous needles melting at $192\text{--}193^{\circ}$:

0.3330 gave 19.6 c.c. N_2 at 17° and 752 mm. $\text{N}=6.91$.

$\text{C}_{27}\text{H}_{30}\text{ON}_2$ requires $\text{N}=7.0$ per cent.

The double Schiff's base therefore gives a monoacetyl and a monobenzoyl derivative.

The action of nitrous acid under various conditions gave a pale yellow, granular precipitate, insoluble in water, but readily soluble in organic solvents, from which it separated as a gum. Analysis of this gave results which were intermediate between the values calculated for mono- and di-nitroso-compounds.

3-Bromo-p-toluidine Aldol Base.

This substance was prepared by mixing 15.5 grams of 3-bromo-p-toluidine with 450 c.c. of 5 per cent. hydrochloric acid, after which about 500 c.c. of water were introduced to clear the solution of precipitated hydrochloride. Eleven c.c. of acetaldehyde were then poured in slowly with shaking. After eighteen hours a slight precipitate was usually formed and 5.5 c.c. more aldehyde were added, the mixture being allowed to remain for four hours more. It was then filtered through glass-wool, 80 c.c. of light petroleum added, and the liquid neutralised by potassium hydroxide with vigorous shaking.

The aldol base separated between the two layers, and after an hour was collected, washed with light petroleum, and crystallised from alcohol, from which it separated in needles melting at $144\text{--}145^{\circ}$. The substance was practically pure, and no trace of an isomeride could be discovered:

0.1605 gave 0.3030 CO_2 and 0.0745 H_2O . $\text{C}=51.5$; $\text{H}=5.6$.

$\text{C}_{11}\text{H}_{14}\text{ONBr}$ requires $\text{C}=51.6$; $\text{H}=5.47$ per cent.

The base is unaffected either by sodium and alcohol or by the aluminium-mercury couple and sodium hydroxide solution.

The *hydrochloride* obtained by precipitation from ether melted at 123° , and from it the base could be recovered unchanged.

There is no reaction with benzoyl chloride by the Schotten-Baumann method, nor yet in pyridine solution.

The *acetyl* derivative of the bromo-*p*-toluidine aldol base is formed in pyridine solution, and separates from alcohol in diamond-shaped plates melting at $83-85^{\circ}$:

0.1505 gave 0.2880 CO_2 and 0.0771 H_2O . $\text{C}=52.2$; $\text{H}=5.66$.

0.3023 „ 12.0 c.c. N_2 at 17° and 752 mm. $\text{N}=4.67$.

$\text{C}_{13}\text{H}_{16}\text{O}_2\text{NBr}$ requires $\text{C}=52.3$; $\text{H}=5.37$; $\text{N}=4.7$ per cent.

The compound is therefore a monoacetyl derivative.

The Nitroso-derivative of Bromo-p-toluidine Aldol Base.

This substance separated from alcohol in small, yellow needles, melting at $136-137^{\circ}$:

0.2045 gave 0.3440 CO_2 and 0.0855 H_2O . $\text{C}=45.9$; $\text{H}=4.65$.

$\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}_2\text{Br}$ requires $\text{C}=46.3$; $\text{H}=4.57$ per cent.

The *acetylnitroso*-compound of the bromo-*p*-toluidine aldol base separates from alcohol in small, yellow plates, melting at $136-137^{\circ}$:

0.1792 gave 13.7 c.c. at 14° and 748 mm. $\text{N}=8.78$.

$\text{C}_{13}\text{H}_{15}\text{O}_3\text{N}_2\text{Br}$ requires $\text{N}=8.57$ per cent.

Double Schiff's Base of Bromo-p-toluidine.

The precipitate which separated from the reaction mixture on keeping was found to be the double Schiff's base, but it was better prepared as described below.

To 15.5 grams of bromo-*p*-toluidine dissolved in 500 c.c. of alcohol, 5.5 c.c. of acetaldehyde were added. After two days, no change having occurred, a few drops of concentrated hydrochloric acid were added. After one day a crystalline precipitate melting at $135-138^{\circ}$ appeared. After recrystallisation from petroleum it melted at $144-146^{\circ}$, and the mixture with the aldol base of bromo-*p*-toluidine melted at $126-130^{\circ}$:

0.1882 gave 0.3490 CO_2 and 0.0798 H_2O . $\text{C}=50.6$; $\text{H}=4.7$.

$(\text{C}_9\text{H}_{10}\text{NBr})_2$ requires $\text{C}=50.9$; $\text{H}=4.72$ per cent.

Therefore, although a diacetyl compound is not formed, the aldol base is capable of reacting as if it contained both an NH- and an OH-group .

ψ -Cumidine Aldol Base.

From the product of the action of acetaldehyde on ψ -cumidine in hydrochloric acid only one of the two isomeric aldol bases which are formed (Trans., 1910, **97**, 643) could be isolated pure in

sufficient quantity with which to work. This, the β -aldol base, was crystallised from benzene and light petroleum, from which it separated in colourless needles melting at 110—112°.

The Benzoyl Derivative of the β - ψ -Cumidine Aldol Base.

The aldol base was treated with benzoyl chloride in pyridine solution, and yielded a substance which crystallises from alcohol in fine needles melting at 240—241°:

0.3228 gave 12.7 c.c. N_2 at 16° and 745 mm. $N=4.59$.

$C_{20}H_{23}O_2N$ requires $N=4.53$ per cent.

The compound is therefore a monobenzoyl derivative.

Acetyl chloride in pyridine solution seems to have little or no action on the aldol base, as the reaction mixture was completely soluble in acid.

The *nitroso*-compound of the β - ψ -cumidine aldol base was prepared in the usual way and crystallised from ether, when it separated in stumpy prisms and plates melting at 110—112°:

0.2667 gave 26.8 c.c. N_2 at 19° and 759 mm. $N=11.8$.

$C_{13}H_{18}O_2N_2$ requires $N=12.0$ per cent.

The compound is therefore a mononitroso-derivative.

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UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.