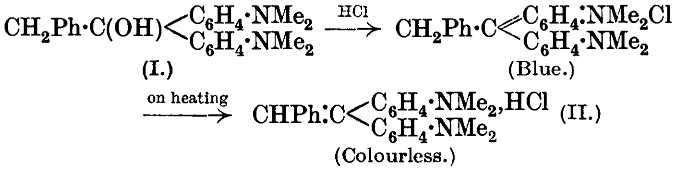
CCXCI.—*Reactions of Sodium Compounds of Aromatic Ketones. Part II. Their Reaction with Methyl and Methylene Groups and their Products of Decomposition.*

By Ernest Harry Rodd and Frank William Linch.

In the preceding paper, it was shown that Michler's ketone and its ethyl homologue combine with sodium in an indifferent solvent to form ketyl compounds which react with aryl chlorides to form triarylcarbinols. Further examination of these ketyl compounds has shown that they are remarkably reactive and that by their means syntheses of a hitherto unrecorded type can be effected. In the course of experiments on the action of sodium on Michler's ketone in toluene solution, a product was obtained in considerable quantity which was eventually proved to be *pp'*-tetramethyldiaminodiphenylbenzylcarbinol, and could only have been produced by the action of the ketyl compound on the methyl group of the toluene. This compound was found to be identical with that obtained as a by-product in the preparation of a triarylcarbinol from Michler's ketone and *o*-chlorotoluene by the action of sodium in toluene solution (Part I). Further experiments showed that the ketyl compound readily reacts with methyl and methylene groups which are generally only attacked by powerful oxidising agents. By this reaction we have been able to prepare with facility a number of new compounds which would be obtainable by known methods only with considerable difficulty.

The Reaction between Michler's Ketone and Toluene in the Presence of Sodium.—It has been shown by previous workers (see Part I) that benzophenone and other aromatic ketones form disodio-compounds, $CR_2(ONa)Na$. If a similar compound were formed by Michler's ketone, it should give, when decomposed by water, Michler's hydrol (tetramethyldiaminobenzhydrol). We attempted to prepare the hydrol by heating Michler's ketone in toluene solution with two atomic proportions of sodium, and obtained, besides the expected hydrol and other by-products which will be discussed later, a considerable yield of pp'-*tetramethyldiaminodiphenylbenzylcarbinol* (I). When benzene was used as solvent instead of toluene, no trace of this compound was formed.

The evidence for the constitution of the compound is as follows. Analysis indicated the formula $C_{24}H_{28}ON_2$, and a molecular-weight determination in camphor gave 350 (calc., 360). The compound shows the properties of a colour base, giving deep blue solutions when dissolved in dilute mineral or acetic acids, but when the solution is heated the colour disappears. This colour change is due to the formation of a new base having the composition $C_{24}H_{26}N_2$, which has been identified as ββ-*tetramethyldiaminodiphenylstyrene* (II), m. p. 135°. The new base is evidently formed from the first by the loss of the elements of water, and since salt formation first occurs, the formation of the styrene may be represented thus :



$$CH_2Ph\cdot C(OH)<\begin{matrix}C_6H_4\cdot NMe_2\\ C_6H_4\cdot NMe_2\end{matrix} \xrightarrow{HCl} CH_2Ph\cdot C<\begin{matrix}C_6H_4{:}NMe_2Cl\\ C_6H_4\cdot NMe_2\end{matrix}$$

(I.) (Blue.)

$$\xrightarrow{\text{on heating}} CHPh{:}C<\begin{matrix}C_6H_4\cdot NMe_2,HCl\\ C_6H_4\cdot NMe_2\end{matrix} \quad (II.)$$

(Colourless.)

By oxidation of the tetramethyldiaminodiphenylbenzylcarbinol with lead peroxide in dilute hydrochloric acid in the cold, phenylacetic acid is obtained, whilst oxidation of the styrene compound readily gives first a greenish-blue dyestuff and then benzaldehyde. The styrene compound is stable to boiling alcoholic potassium hydroxide, but when fused with potassium hydroxide it gives Michler's ketone. All these reactions confirm the constitutions assigned to the two new bases.

The conversion of the carbinol into the styrene derivative is best effected by boiling it for a short time with 10% hydrochloric acid; when the solution is cooled the styrene separates as a sparingly soluble, white, crystalline *dihydrochloride.* This property facilitates the detection of the carbinol and the purification of the styrene. The dihydrochloride is hydrolysed by water with precipitation of the base. A characteristic property of this styrene, and of other similar compounds which we have made, is its oxidation in acetic or dilute mineral acid to an intense blue dyestuff by chromic acid or lead peroxide. The fact that solutions of the carbinol prepared in the cold do not give this reaction but that they give it after heating shows that the conversion of the carbinol into the styrene does not proceed readily in the cold. The cold oxidation of the carbinol to phenylacetic acid illustrates the same point.

When the identity of the product obained from toluene had been established, experiments were extended, and it was found that *p*-xylene gave a similar product with Michler's ketone, whilst tetraethyldiaminobenzophenone reacted similarly with toluene in the presence of sodium.

Reaction with Substances containing the Methylene Group.—Regarding the formation of a benzyl derivative from toluene as due to oxidation of the methyl group with simultaneous formation of benzhydrol, we considered that a substance containing a readily oxidisable methylene group should also react with the sodium derivative of Michler's ketone. As a convenient substance with which to experiment we chose *pp'*-tetramethyldiaminodiphenylmethane. When this was heated with Michler's ketone and sodium in benzene solution, we obtained without difficulty a good yield of *octamethyltetra-aminotetraphenylethanol*,

$$(NMe_2{\cdot}C_6H_4)_2C(OH){\cdot}CH(C_6H_4{\cdot}NMe_2)_2 \text{ (III)},$$

which by dehydration with sulphuric acid gave octamethyltetraaminotetraphenylethylene, which has been described by Gattermann (*Ber.*, 1895, **28**, 2876) and Willstätter and Goldmann (*Ber.*, 1906, **39**, 3765). This observation confirmed our conclusions with regard to the reaction products from toluene, and suggested that the reaction might be of general application. To obtain further confirmatory evidence, carbinols were prepared from (*a*) Michler's ketone and tetraethyldiaminodiphenylmethane, and (*b*) tetraethyldiaminobenzophenone and tetramethyldiaminodiphenylmethane, and the two carbinols, $(NMe_2{\cdot}C_6H_4)_2C(OH){\cdot}CH(C_6H_4{\cdot}NEt_2)_2$ (IV) and $(NEt_2{\cdot}C_6H_4)_2C(OH){\cdot}CH(C_6H_4{\cdot}NMe_2)_2$ (V) were shown to give the same ethylene compound by dehydration with sulphuric acid.

Other substances of diverse character containing the methylene group, which have been found to react with the ketyl compound, are acenaphthene and fluorene. In each case, the expected compound was obtained without difficulty in benzene solution. Tetrahydronaphthalene, however, failed to react.

Decomposition Products of the Sodium Ketyl Compound and the Mechanism of its Reaction with Methyl and Methylene Groups.—To explain the ready attack of the ketyl compound on methyl and methylene groups, it is simplest to assume that the radicals $CR_2(ONa){\cdot}$ (where $R = NMe_2{\cdot}C_6H_4$) are the active agents. Since Michler's hydrol is always a product, the reaction, in the case of toluene, assumes the form $2CR_2(ONa){\cdot} + CH_3Ph = CR_2H(ONa) + CR_2(ONa){\cdot}CH_2Ph$. For this reaction, only one atom of sodium should be required per mol. of ketone, but when only one atomic proportion of sodium was heated with the ketone in toluene solution, although in the course of 2 hours the whole of the sodium had disappeared, yet no benzyl compound was formed. This observation led us to make a more careful study of the reaction.

With 0·95 atomic proportion of sodium, in two experiments, after heating in a closed vessel for 2 hours and 16 hours, respectively, identical results were obtained: no benzyl carbinol was found, about one-third of the ketone was recovered, and the products included about 0·1 mol. of Michler's hydrol, 0·2 mol. of dimethylaminobenzoic acid, and other bases, including much crystal violet. These, together with dimethylaniline, are the usual products under similar conditions.

When the sodium is increased to 1·5 atomic proportions, a maximum yield of benzylcarbinol is obtained, and sodium remains unchanged at the end; no ketone is recovered. The same result is obtained by using 2 atomic proportions of sodium. A typical experiment, with 1 mol. of Michler's ketone, gave approximately 0·37 mol. of tetramethyldiaminodiphenylbenzylcarbinol, 0·30 mol. of hydrol, 0·08 mol. of dimethylaminobenzoic acid, and 0·11 mol. of colour base.

When benzene is used as solvent, with 2 atoms of sodium, the principal product is Michler's hydrol, with a fair amount of colour base.

During the reaction, the solution gradually assumes an intensely greenish-blue colour, but if air is passed through the apparatus, no blue colour is produced, no hydrol is obtained, and most of the ketone is recovered unchanged, but some dimethylaminobenzoic acid and crystal violet are formed, together with a much redder dyestuff, probably indicating oxidation of the dimethylamino-groups of crystal violet.

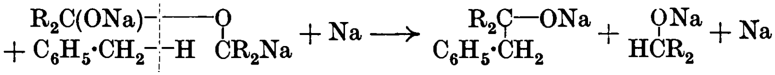
If a chloro-compound is added to the reaction mixture, when only one atomic proportion of sodium or less is used, no blue colour appears, but the formation of dye base proceeds at once (*e.g.*, of malachite green, from chlorobenzene), and only traces of the above by-products are formed.

Whilst we feel that more data are required before an entirely satisfactory explanation can be given of all the above observations, we put forward the following discussion tentatively. First, with regard to the colour of the solution obtained when sodium dissolves in a solution of the ketone, it has been freely assumed by Schlenk that free radicals of the type $R_2C(ONa)\cdot$ are coloured, just as Gomberg assumes that free radicals, $R_3C\cdot$, have colour. If this assumption be accepted, then free radicals must always be present in our toluene solutions of the ketyl compound at all stages of the reaction, but the quantity of free radical present may be very small, since traces of oxygen rapidly decolorise the solution. In the presence of a chloro-compound, no colour ever appears, and since the formation of a triarylcarbinol starts at once, it is probably the monosodio-derivative of the ketone which attacks the chloro-compound, as suggested by Schlenk and Weickel to explain the action between sodiobisdiphenylyl ketone and methyl iodide (*Ber.*, 1911, **44**, 1182):

$$2R_2C(ONa)\cdot + R'Cl \begin{array}{l} \nearrow R_2R'C(ONa) \xrightarrow{H_2O} R_2R'C(OH) \\ \searrow R_2CCl(ONa) \longrightarrow R_2CO + NaCl \end{array}$$

It is not necessary then to assume the formation of a disodio-compound of the ketone (compare Part I).

The non-formation of benzyl compound when only one atom of sodium is used may be due to the greater tendency of a monosodio-radical to combine with another mol. of ketone than to attack a methyl group. We suggest that an intermediate compound, probably of the type $R_2C(ONa){\cdot}O{\cdot}CR_2Na$, is formed,* combination taking place through the oxygen atom, rather than between two carbon atoms. It has been shown recently by Schorigen (*Ber.*, 1926, **59**, 2510) that when sodium acts on complex ethers the point of attack is the oxygen atom. Hence, when more than one atomic proportion of sodium is available, the intermediate compound would be attacked with formation of active free radicals which would attack the toluene :



$$\begin{array}{l} R_2C(ONa)\text{-}\vdots\text{—}O \\ +\ C_6H_5{\cdot}CH_2\text{-}\vdots\text{-}H\ \ CR_2Na \end{array} + Na \longrightarrow \begin{array}{l} R_2C\text{—}ONa \\ C_6H_5{\cdot}CH_2 \end{array} + \begin{array}{c} ONa \\ HCR_2 \end{array} + Na$$

It would appear that the additional sodium acts catalytically, and this agrees with the experimental results, as far as we can interpret them. Owing to side reactions, however, it has not been possible to determine how much of the sodium employed takes part in this reaction.

The observation that oxygen destroys the blue colour formed by the addition of sodium to the ketone, mainly with re-formation of the ketone, agrees with Schlenk's observations on simple aromatic ketones (*Ber.*, 1914, **47**, 487) :

$$2R_2C(ONa){\cdot} + O_2 \longrightarrow R_2C(ONa){\cdot}O{\cdot}O{\cdot}CR_2(ONa) \longrightarrow 2R_2C{:}O + Na_2O_2.$$

The formation of *p*-dimethylaminobenzoic acid, crystal-violet base, and dimethylaniline as by-products must be attributed to a general loosening of the bonds between the aryl radicals and the keto-carbon atom in the ketyl compound. Since these products are formed to the greatest extent when there is a deficiency of sodium, they are probably the result of internal rearrangement in a complex molecule or radical, *e.g.*, $CR_2(ONa){\cdot}O{\cdot}CR_2{\cdot} \longrightarrow {\cdot}CR(ONa){\cdot}O{\cdot}CR_3 \xrightarrow{+R_2CO} R_2CNa{\cdot}O{\cdot}CR(ONa){\cdot}O{\cdot}CR_3$. The last complex on hydrolysis should give 1 mol. each of Michler's hydrol, dimethylaminobenzoic acid, and crystal-violet base. Undoubtedly we have not yet identified all the by-products, so it is not possible to give a complete picture of the changes taking place. We do not exclude the possibility of the formation of the pinacol, $R_2C(ONa){\cdot}CR_2(ONa)$, but we have as yet no evidence for it.

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* This type of intermediate compound was also suggested by Beckmann and Paul (*Annalen*, 1891, **266**, 1) to explain the formation of benzophenone and benzhydrol from the monosodio-derivative of benzophenone.

EXPERIMENTAL.

The Michler's ketone used for these experiments was the technical product, purified by boiling with very dilute hydrochloric acid and recrystallising the insoluble portion from alcohol. The toluene used was the commercial product, redistilled and dried over sodium.

pp′-*Tetramethyldiaminodiphenylbenzylcarbinol* (I).—In a flask fitted with a sealed stirrer and a reflux condenser were placed 800 c.c. of toluene, 268 g. of Michler's ketone and 46 g. of sodium, and the whole was heated in a bath kept at 100—105° for 12 hours, with continuous stirring. During the heating, the colour of the solution became deep greenish-blue and remained so throughout the experiment. The blue colour is destroyed at once by air. The contents of the flask were cooled, poured off from the unchanged sodium, and treated with ice to hydrolyse the sodium compounds. The whole was then steam-distilled to remove the toluene and dimethylaniline, if any. The bases were filtered from the alkaline aqueous liquor and extracted thoroughly with ether. The residue consisted of nearly pure pp′-*tetramethyldiaminodiphenylbenzylcarbinol*, 131 g., m. p. 185°. (In those experiments in which only 0·95 mol. of sodium is used, the residue at this stage consists of nearly pure unchanged ketone, which is also almost insoluble in ether.) A similar experiment gave 36 g., m. p. 187°, from 67 g. of Michler's ketone. By recrystallisation from toluene the base is obtained in colourless, transparent needles, often pointed at one end only, m. p. 190·5° (Found: C, 79·62; H, 7·79; N, 7·72; *M*, cryoscopic in camphor, 350. $C_{24}H_{28}ON_2$ requires C, 80·00; H, 7·77; N, 7·77%; *M*, 360). The carbinol dissolves in acetic acid with a blue colour, which becomes intense on warming, then quickly fainter, and finally very pale blue.

The other products of the reaction were separated as follows: The alkaline filtrate obtained above was neutralised to precipitate the *p*-dimethylaminobenzoic acid, which was filtered, dried, and weighed. From the solid residue, consisting of carbinol and other bases, the ether had extracted the latter (see above), and this extract was freed from solvent and dissolved in dilute sulphuric acid. A strong solution of sodium hydrogen sulphite was then added, and the mixture warmed at 60°, whereby the Michler's hydrol was converted into *pp*′-tetramethyldiaminodiphenylmethane-ω-sulphonic acid. The solution was made alkaline with sodium hydroxide, filtered from the precipitated bases, and the sodium ω-sulphonate salted out (when dried, it is approx. 80% pure). The bases were extracted with dilute oxalic acid solution (which left a little ketone in those cases where there was a deficiency of sodium, see p. 2181) and the solution yielded a considerable amount of crystal violet oxalate. Other bases (unidentified) were, however, also present.

In one experiment, the dimethylaniline in the recovered toluene was found to be 1·4 g. from 67·0 g. of ketone, and the other products, separated as described above, were 27·0 g. of the benzylcarbinol (m. p. 190°, crude), 5·0 g. of dimethylaminobenzoic acid, about 26 g. of Michler's hydrol, and 8·5 g. of crude crystal-violet base.

An experiment was carried out in which the apparatus was sealed with special care and connected to a manometer, after the required temperature had been attained. There was no evidence of any change of pressure, showing that no gaseous products are formed.

ββ-pp'-*Tetramethyldiaminodiphenylstyrene* (II).—This may be prepared from the crude *pp'*-tetramethyldiaminodiphenylbenzylcarbinol by dissolving 20 g. in 100 c.c. of 2*N*-hydrochloric acid and boiling for ½ hour; on cooling, the solution deposits 20 g. of the *dihydrochloride* of the styrene in soft, shining, colourless needles (Found in crude product: Cl, 16·0. $C_{24}H_{28}N_2Cl_2$ requires Cl, 17·1%). The basification is carried out by suspending the hydrochloride in water and gradually stirring in dilute sodium hydroxide. The *base*, recrystallised from a mixture of acetone and methyl alcohol, forms short, pale yellow prisms, m. p. 135° (Found: C, 84·66, 84·21; H, 7·90, 7·92; N, 8·17. $C_{24}H_{26}N_2$ requires C, 84·21; H, 7·60; N, 8·19%). In a quantitative experiment on the conversion of the pure benzylcarbinol into the styrene, 0·7662 g. of the former gave 0·7250 g. of the latter (theory, 0·728 g.).

Oxidation of pp'-*Tetramethyldiaminodiphenylbenzylcarbinol*.—14·4 G. of the carbinol were dissolved in 350 c.c. of cold *N*-hydrochloric acid. A thin paste of 29 g. of lead peroxide was added gradually to the stirred solution of the carbinol and oxidation was allowed to proceed for some hours at the ordinary temperature. The lead was precipitated with sodium sulphate and the filtrate basified with sodium hydroxide. The alkaline solution was extracted with ether, but the basic products of the oxidation could not be obtained sufficiently pure for identification. The solution was then acidified with dilute hydrochloric acid and again extracted with ether. After removal of the ether, an oily residue was left which solidified on standing (5·1 g.). It was recrystallised twice from hot water, giving large, glistening plates, m. p. 76—77°. This product had all the properties of phenylacetic acid, and its identity was established by comparison (mixed m. p.) with a sample prepared from benzyl cyanide.

Octamethyltetra-aminotetraphenylethanol, (III).—A mixture of 26·8 g. of Michler's ketone, 4·6 g. of sodium, 50 g. of *pp'*-tetramethyldiaminodiphenylmethane, and 100 c.c. of dry benzene was heated at 85—90° for 16 hours with efficient stirring. The sodium was separated and the benzene removed by steam-distillation. The residual white solid was filtered off and boiled out twice with alcohol to remove Michler's hydrol and other impurities. The insoluble white residue (20 g.) was substantially pure *octamethyltetra-aminotetraphenylethanol.* It is sparingly soluble in all neutral organic solvents and is best recrystallised from toluene; colourless needles, m. p. 255° (Found : C, 77·7; H, 8·0; N, 10·7. $C_{34}H_{42}N_4O$ requires C, 78·1; H, 8·0; N, 10·7%). It dissolves in weak mineral acids or glacial acetic acid to give greenish-blue salts which become violet on addition of lead peroxide.

The same method of preparation and the same molecular proportions of materials were used in the following preparations.

αα-4 : 4′-Tetraethyldiaminodiphenyl-ββ-4 : 4′-tetramethyldiaminodiphenylethan-α-ol (V) from *pp′*-tetraethyldiaminobenzophenone and *pp′*-tetramethyldiaminodiphenylmethane : white needles from toluene or alcohol–chloroform, m. p. 228° (Found: N, 9·6. $C_{38}H_{50}N_4O$ requires N, 9·7%).

αα-4 : 4′-Tetramethyldiaminodiphenyl-ββ-4 : 4′-tetraethyldiaminodiphenylethan-α-ol (IV) from *pp′*-tetramethyldiaminobenzophenone and *pp′*-tetraethyldiaminodiphenylmethane : white needles from toluene or alcohol–chloroform, m. p. 229—230° (Found : N, 9·6. $C_{38}H_{50}N_4O$ requires N, 9·7%).

Both compounds dissolve in dilute mineral acids or glacial acetic acid, giving greenish-blue solutions which turn violet on the addition of a little lead peroxide. These ethanol derivatives were converted into the corresponding ethylene compounds by warming with concentrated sulphuric acid.

Octamethyltetra-aminotetraphenylethylene, $(NMe_2{\cdot}C_6H_4)_2C{:}C(C_6H_4{\cdot}NMe_2)_2$.—5 G. of the ethanol were dissolved in 25 c.c. of concentrated sulphuric acid and warmed for ½ hour in a boiling water-bath. The pale green solution was poured into ice water and the base precipitated by the addition of sodium hydroxide as a yellowish-white powder; yield 4·7 g. It crystallises from acetone–methyl alcohol in greenish-yellow needles, m. p. 314—316° (Gattermann, *Ber.*, 1895, **28**, 2876, gives m. p. 310—315°) (Found : N, 11·1. Calc. for $C_{34}H_{40}N_4$: N, 11·1%). It forms colourless salts when dissolved in acids, but the solutions turn violet on the addition of a little lead peroxide.

αα-4 : 4′-Tetraethyldiaminodiphenyl-ββ-4 : 4′-tetramethyldiaminodiphenylethanol and αα-4 : 4′-tetramethyldiaminodiphenyl-ββ-4 : 4′-tetraethyldiaminodiphenylethanol when warmed with concentrated sulphuric acid gave the same product, *viz.*, *αα-4 : 4′-tetraethyldiaminodiphenyl-ββ-4 : 4′-tetramethyldiaminodiphenylethylene,* pale yellow needles from alcohol–chloroform, m. p. 212°. The identity was established by mixed melting-point and nitrogen determinations (Found: N, 10·0, in each case. $C_{38}H_{48}N_4$ requires N, 10·0%).

4 : 4′-*Tetramethyldiaminodiphenylacenaphthenylcarbinol*,

$$(NMe_2\cdot C_6H_4)_2C(OH)\cdot C_{12}H_9.$$

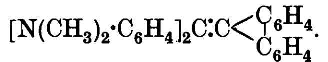
—A well-agitated mixture of 26·8 g. of Michler's ketone, 4·6 g. of sodium, 30 g. of acenaphthene, and 100 c.c. of dry benzene was heated at 85—90° for 16 hours. The excess of sodium was separated and the benzene removed by steam-distillation. The residual crystalline mass was filtered off and boiled several times with alcohol to remove impurities. The white, insoluble residue (12 g.) was recrystallised from toluene; colourless needles, m. p. 232° (Found: N, 6·7. $C_{29}H_{30}ON_2$ requires N, 6·6%). It dissolves in dilute mineral acids or glacial acetic acid to reddish-blue solutions. These solutions are almost decolorised by boiling, and on the addition of a little lead peroxide the resulting solution assumes a violet colour.

4 : 4′-*Tetramethyldiaminodiphenylmethyleneacenaphthene*,

$$(NMe_2\cdot C_6H_4)_2C{:}C_{12}H_8.$$

—Since concentrated sulphuric acid sulphonates the acenaphthene nucleus, in this case the ethylene derivative was prepared by boiling 5 g. of the ethanol for an hour with aqueous hydrochloric acid. On cooling, a crystalline *hydrochloride* was deposited in fine, white needles. The *base* was obtained as a greenish-yellow powder by basifying with sodium hydroxide. The dried product (4·7 g.) was recrystallised from chloroform–alcohol; pale yellow plates, m. p. 209° (Found: N, 7·0. $C_{29}H_{28}N_2$ requires N, 6·9%). It dissolves in acetic acid to a colourless solution which turns violet on addition of lead peroxide.

4 : 4′-*Tetramethyldiaminodiphenylmethylenefluorene*,



$$[N(CH_3)_2\cdot C_6H_4]_2C{:}C{<}\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}.$$

—A mixture of 13·4 g. of Michler's ketone, 2·3 g. of sodium, 20 g. of fluorene, and 50 c.c. of dry benzene was heated with stirring at 85—90° for 16 hours. The unchanged sodium (0·5 g.) was separated and the benzene removed by steam distillation. The residual, orange, crystalline product was boiled three times with alcohol and the insoluble residue (8·5 g.) was recrystallised first from toluene and finally from chloroform–alcohol; pale yellow needles, m. p. 239—240° (Found: N, 6·7. $C_{30}H_{28}N_2$ requires N, 6·7%). It dissolves in dilute mineral acids or acetic acid to a pale yellowish-green solution which turns blue on addition of lead peroxide. In this case, dehydration of the carbinol to the ethylene derivative has occurred at some stage which has not been determined.

The analyses recorded in Parts I and II were carried out by Mr. W. H. Cliffe, whose help we gratefully acknowledge. The work was carried out in the Research Department of the British Dyestuffs Corporation, Ltd., to whom our thanks are due for permission to publish it.

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Addendum.—Since the above work was completed, a paper by Madelung and Völker has appeared (*J. pr. Chem.*, 1927, **115**, 24), in which the formation of *pp'*-tetramethyldiaminodiphenylbenzylcarbinol and of *pp'*-tetramethyldiaminodiphenylstyrene from Michler's ketone and magnesium benzyl chloride is described, the styrene being the principal product. The m. p.'s are stated to be 173° and 129°, respectively, whereas our m. p.'s are 190·5° and 135°. The above authors' compounds are evidently impure, and are most probably contaminated with unchanged ketone, since our observations have shown that with Michler's ketone the Grignard reaction only proceeds to a very limited extent. It is to be noted that earlier workers, by the action of magnesium alkyl halides on Michler's ketone, never obtained carbinols, but always the corresponding ethylene derivative. Madelung and Völker state that the carbinol and the styrene both give the same blue colour in acetic acid (*loc. cit.*, pp. 29, 41). This does not agree with our observations; we find that the former gives a very intense blue colour with cold acetic or with one equiv. of dilute mineral acid, comparable in intensity with the colour given by a true triphenylmethane-dye base, whilst the styrene gives a very weak colour. When the intensely coloured solution of the carbinol in acid is heated, the colour gradually disappears and finally approximates in intensity to that given by the styrene.