CCXC.—*Reactions of Sodium Compounds of Aromatic Ketones. Part I. Synthesis of Triarylcarbinols and of Triarylmethane Dyes.*

By Ernest Harry Rodd and Frank William Linch.

It has been known for many years that aromatic ketones form compounds with metallic sodium in an inert solvent. The literature of the subject, from the original observation by Beckmann and Paul (*Annalen*, 1891, **266**, 1) that benzophenone forms a coloured compound with sodium, is usefully summarised in *Ann. Reports*, 1925, **22**, 123—126. Workers in this field have hitherto confined themselves to unsubstituted ketones such as benzophenone and phenyl diphenylyl ketone, and have studied the decomposition products of the sodium ketyls with water, oxygen, iodine, and methyl iodide with the object of elucidating their structure. Schlenk and his co-workers state that benzophenone forms a blue monosodio-derivative, probably containing tervalent carbon, and a violet disodio-derivative, $CPh_2(ONa)Na$; the disodio-compound of phenyl diphenylyl ketone was actually isolated (*Ber.*, 1914, **47**, 487).

We were attracted by the possibility of preparing triarylmethane dyes by the interaction of the sodio-derivatives of suitably substituted ketones with halogenated aromatic compounds. The observation by Frey (*Ber.*, 1895, **28**, 2514), that triphenylcarbinol is formed from benzophenone and bromobenzene in ether in the presence of sodium, made the project appear feasible. Blicke had also observed the formation of triphenylcarbinol from benzaldehyde, bromobenzene, and sodium, and he assumed the intermediate formation of benzophenone (*J. Amer. Chem. Soc.*, 1924, **46**, 2560).

Experiments at once showed that Michler's ketone, *pp'*-tetramethyldiaminobenzophenone, when heated with chlorobenzene in the presence of sodium, gave, after treatment of the product with water, the expected carbinol, which was readily converted into the well-known dyestuff, malachite green. The formation of the sodio-compound of the ketone is extremely slow in ether on account of the low solubility of the ketone and the low b. p. of the solvent, but in benzene or toluene at 80—100° the reaction is much more rapid, and these solvents are suitable for carrying out the synthesis. The reaction has been extended to a number of chlorinated hydrocarbons, including *o*-chlorotoluene, 4-chloro-*m*-xylene, chloro-*p*-xylene, α- and β-chloronaphthalene, and chloroanisoles. In place of Michler's ketone, *pp'*-tetraethyldiaminobenzophenone has been used; with chlorobenzene, this gives the carbinol corresponding with the dye, brilliant green. The condensation of the ketone with the chloro-compound requires two atoms of sodium per mol. of ketone for its completion; by the use of this proportion, with a slight excess of chloro-compound, there is little unchanged ketone and no sodium left at the end of the reaction. The reaction may therefore be expressed by the equations :

$$R_2CO + 2Na = R_2C(ONa)Na;$$
$$R_2C(ONa)Na + R'Cl = R_2R'C(ONa) + NaCl.$$

From our subsequent study of the ketyl compound, however, it is doubtful whether there is ever present any appreciable concentration of the disodio-compound (see following paper).

By means of this reaction several new dyes, not hitherto described because not readily obtainable by known methods, have been prepared. The yields are generally substantial; the carbinols obtained have in some instances been difficult to purify, whilst in other instances good yields of the pure triarylcarbinol were readily obtained. The yield and quality of carbinol obtained vary with the reaction conditions and with the mobility of the reacting chlorine atom. As by-products, diaryls may be formed by the reaction $2RCl + 2Na = R{\cdot}R + 2NaCl$. On the other hand, the ketyl compound may undergo decomposition with formation of by-products, and may even react with toluene when this is used as solvent. The decomposition of the ketyl compound and its reactions will be discussed in Part II (following paper).

Attempts have been made to obtain dye-bases by heating the ketyl compounds with many other benzenoid chloro-compounds. The presence of groups which may be attacked by sodium, such as nitro- and amino-groups, is always inimical to the reaction. Dichloro-compounds, such as *p*-dichlorobenzene and 4 : 4′-dichlorodiphenyl, gave dye-bases, but difficulty was experienced in purifying them; whilst more highly chlorinated compounds, such as tetrachlorotoluene, only gave traces of dye-base, under the conditions used.

In purifying some of the carbinols obtained, it was observed that, when the dye salts were basified with ammonia, the basified product had an abnormally high nitrogen content. It was eventually proved that basification with ammonia gave, not the carbinol, but the corresponding amine, *e.g.*, $C(NH_2)(C_6H_4{\cdot}NMe_2)_2(C_6H_4Me)$. A similar observation has been made by Noelting and Saas (*Ber.*, 1913, **46**, 953), who obtained the amine $C(NH_2)(C_6H_4{\cdot}NMe_2)_3$ by the action of ammonia on an aqueous solution of crystal violet.

EXPERIMENTAL.

pp′-*Tetramethyldiaminodiphenyl*-o-*tolylcarbinol*, $[(CH_3)_2N{\cdot}C_6H_4]_2C(OH){\cdot}C_6H_4{\cdot}CH_3$. —A mixture of 13·4 g. of *pp*′-tetramethyldiaminobenzophenone, 2·3 g. of sodium, 7 g. of *o*-chlorotoluene, and 50 c.c. of dry toluene was heated in a closed flask provided with a stirrer at 100—105° for 16 hours. The ketone dissolved to a pale yellow solution, but as the reaction proceeded the mixture darkened and a light brown, crystalline powder gradually separated. A little water was added to the reaction mixture, and the toluene and any excess of *o*-chlorotoluene were removed by steam-distillation. The brown, gummy residue of impure carbinol became semi-solid on standing. From the aqueous liquor, a small quantity of *p*-dimethylaminobenzoic acid was obtained by neutralisation with acetic acid. The crude carbinol was extracted with ligroin, filtered from insoluble residue, and the solution evaporated. The carbinol so obtained was dissolved in 100 c.c. of boiling 10% oxalic acid solution and filtered from insoluble matter. The oxalate separated on cooling in green, bronzy crystals. These were redissolved in 100 c.c. of hot water and a further amount of insoluble matter was filtered off. This latter contained a little unchanged Michler's ketone. The residue left when the crude carbinol was extracted with ligroin consisted mainly of a product crystallising from toluene in colourless needles, m. p. 190°, which has been identified as *pp'*-tetramethyldiaminodiphenylbenzylcarbinol, $[(CH_3)_2N\cdot C_6H_4]_2C(OH)\cdot CH_2\cdot C_6H_5$. The mode of formation and properties of this substance will be discussed in Part II. The solution of the oxalate of the carbinol was basified with excess of sodium hydroxide. The blue precipitate of pp'-*tetramethyldiaminodiphenyl-*o*-tolylcarbinol* was filtered, washed, dried, boiled out with ligroin, and recrystallised from alcohol. It forms small colourless needles, m. p. 132·5°, becoming light blue on exposure to air. Yield, 8 g. (Found : N, 7·8. $C_{24}H_{28}N_2O$ requires N, 7·8%). The carbinol is moderately soluble in the cold in the usual organic solvents, and readily soluble in warm alcohol and toluene.

When the oxalate is basified with ammonia, pp'-*tetramethyldiaminodiphenyl-*o*-tolylmethylamine* is obtained, which, when recrystallised from ligroin–toluene, has m. p. 163° (Found : N, 11·7. $C_{24}H_{29}N_3$ requires N, 11·7%).

In concentrated sulphuric or hydrochloric acid, the carbinol gives a reddish-brown solution which turns green on addition of water, finally changing to blue. The oxalate gives an intense blue solution in water and a greenish-blue solution in alcohol. Aqueous solutions of the salts of the carbinol dye tannin-mordanted cotton greenish-blue.

Reduction of the carbinol with zinc and 2*N*-hydrochloric acid gave *pp'*-tetramethyldiaminodiphenyl-*o*-tolylmethane, white, glistening needles from alcohol, m. p. 102° (compare Noelting and Gerlinger, *Ber.*, 1906, **39**, 2042).

4-Chloro-*m*-xylene condenses similarly with Michler's ketone to give pp'-*tetramethyldiaminodiphenyl-*m*-4-xylylcarbinol.* This base crystallises from alcohol in small, colourless needles, m. p. 145°.

pp'-*Tetramethyldiaminodiphenyl-*p*-anisylcarbinol*,

$(NMe_2\cdot C_6H_4)_2C(OH)\cdot C_6H_4\cdot OMe$.

—A mixture of 13·4 g. of Michler's ketone, 2·3 g. of sodium, 7·5 g. of *p*-chloroanisole, and 50 c.c. of toluene was heated in a boiling water-bath for 12—16 hours in a closed flask with a stirrer. The crude carbinol, obtained by treating the product with water and removing toluene by steam-distillation, was converted into the *oxalate*, which crystallised in bronzy nodules. These were redissolved in hot water, filtered from a little ketone, and the solution was basified with ammonia; the bluish-white *carbinol* was filtered off, washed with a little alcohol, and dried. It separated from ligroin partly as a gum and partly as crystals; yield, 5·8 g. The latter crystallised from benzene–ligroin in almost colourless needles, m. p. 153° (Found: C, 76·6; H, 7·4; N, 7·5. $C_{24}H_{28}O_2N_2$ requires C, 76·6; H, 7·4; N, 7·4%). The carbinol dissolves in organic acids, *e.g.*, oxalic and acetic acids, to give intense green solutions. Mineral acids give brown solutions turning green on dilution with water. Solutions of the salts dye tannin-mordanted cotton greenish-blue.

pp′-*Tetramethyldiaminodiphenyl*-β-*naphthylcarbinol*.—A mixture of 6·7 g. of Michler's ketone, 1·2 g. of sodium, 4·5 g. of β-chloronaphthalene, and 30 c.c. of dry toluene was stirred for 4½ hours in a boiling water-bath. A dark-coloured product separated during the heating, and on cooling, a copious, grey, crystalline deposit was obtained. This was filtered, washed with a little toluene, and warmed with water; the crude carbinol then remained as a yellow, crystalline powder. The main impurities are unchanged ketone, β-chloronaphthalene, and an appreciable amount of ββ-dinaphthyl. The crude carbinol was purified by conversion into the crystalline oxalate and basification with ammonia; yield, 4·1 g. The *carbinol* crystallises best from aqueous pyridine (in needles) or from benzene–ligroin (in prisms), m. p. 181° (Found: N, 7·0. $C_{27}H_{28}N_2O$ requires N, 7·1%).

pp′-*Tetraethyldiaminodiphenyl*-β-*naphthylcarbinol*.—The reaction proceeds similarly with equivalent amounts of tetraethyldiaminobenzophenone, β-chloronaphthalene, and sodium. In this case the carbinol is easy to purify owing to its sparing solubility in hot alcohol, the impurities being readily soluble. The alcohol-extracted *carbinol*, recrystallised from benzene–ligroin, forms colourless plates, m. p. 177° (Found: N, 6·2. $C_{31}H_{36}N_2O$ requires N, 6·2%). Yield, 51%. The carbinol forms green salts with acids, and aqueous solutions of such salts dye tannin-mordanted cotton a bright yellowish-green.

pp′-*Tetramethyldiaminodiphenyl*-α-*naphthylcarbinol*.—This carbinol is obtained when α-chloronaphthalene is heated with Michler's ketone and sodium. Owing to the greater reactivity of the α-chlorine atom, a much larger proportion of αα-dinaphthyl is formed and this product collects in the portion insoluble in oxalic acid. The crude carbinol is best purified by solution in hot toluene and partial precipitation with ligroin. pp′-*Tetramethyldiaminodiphenyl*-α-*naphthylcarbinol* crystallises from acetone in colourless needles, m. p. 167° (Found: N, 7·0. $C_{27}H_{28}N_2O$ requires N, 7·1%). pp′-*Tetramethyldiaminodiphenyl*-α-*naphthylmethylamine*, obtained by basifying the oxalate with ammonia, has m. p. 186° (Found: N, 10·3. $C_{27}H_{29}N_3$ requires N, 10·6%).

BLACKLEY, MANCHESTER.

[*Received, June 8th*, 1927.]