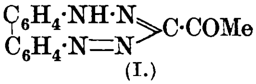
CIII.—*Corrections in the Chemistry of Diphenyl Derivatives of the "Kaufler" Type, and the Formation of Dibenzoctdiazines.*

By Raymond James Wood Le Fèvre.

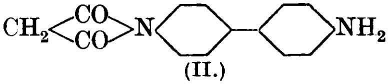
The reinvestigation of compounds of the type cited by Kaufler (*Annalen*, 1907, **351**, 151; *Ber.*, 1907, **40**, 3250), begun by Le Fèvre and Turner (J., 1926, 2476) for such as were derivatives of benzidine, was extended by Kuhn, Jacob, and Furter (*Annalen*, 1927, **455**, 254) to include those derived from *NN′*-dialkylbenzidines, 4 : 4′-diaminodiphenylmethane, and diaminonaphthalene. There remained unexamined, however, the "malonylbenzidine" of Remfry (J., 1911, **99**, 610), "thiocarbonyl- and carbonyl-dianisidines" (Starke, *J. pr. Chem.*, 1899, **59**, 216), "carbonyl-*o*-tolidine" and "oxalyl-*o*-tolidine" (Taussig, *Monatsh.*, 1904, **25**, 375), and "*cyclo*formazyl methyl ketone" (formulated as I by Wedekind, *Annalen*, 1898, **300**, 251).

The first three of these substances react with salicylaldehyde to give, in each case, a *salicylidene* derivative (compare Le Fèvre and Turner, *loc. cit.*), indicating the presence of a free amino-group (or groups). Remfry's compound is probably (II), since it forms a *sulphate* and its salicylidene derivative is a well-defined crystalline substance (compare salicylidenemonophthalylbenzidine, Le Fèvre and Turner, *loc. cit.*).

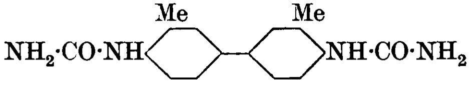


$$\left.\begin{array}{l} C_6H_4\cdot NH\cdot N \\ C_6H_4\cdot N{=}N \end{array}\right> C\cdot COMe$$

(I.)



(II.)

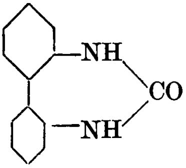


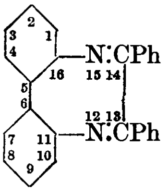
(III.)

"Carbonyl-*o*-tolidine" is evidently (III), since (1) it is formed in best yield by heating 1 mol. of *o*-tolidine with 2 mols. of carbamide and (2) it can be obtained by mixing solutions of *o*-tolidine hydrochloride and potassium cyanate. Taussig's "oxalylbenzidine" does not react with salicylaldehyde, and analysis shows it to be the 4 : 4′-*di-*

ethyloxamido-3 : 3′-*dimethyldiphenyl* to be expected from the interaction of ethyl oxalate with *o*-tolidine, which should resemble that of ethyl oxalate with benzidine (Le Fèvre and Turner, J., 1928, 245). Wedekind's directions for the preparation of " *cyclo*formazyl methyl ketone " have been carried out on several occasions, but the products were always coloured inseparable mixtures apparently containing phenolic impurities.

(IV.)





(V.)

The condensation products of 2 : 2′-diaminodiphenyl with carbamide and with benzil (Niementowski, *Ber*., 1901, **34**, 3330) are evidently *NN*′-carbonyl-2 : 2′-diaminodiphenyl (IV) and 13 : 14-diphenyldibenzoct-12 : 15-diazine (V), respectively, since, like 13 : 14-(oo′-*diphenylylene*)*dibenzoct*-12 : 15-*diazine* and 3 : 8-*dibromo*-13 : 14-(oo′-*diphenylylene*)*dibenzoct*-12 : 15-*diazine*, they are inert towards boiling salicylaldehyde, do not form sulphates, and, in addition, are obtained in maximum yields when the reactants are taken in molecular proportion. NN′-*Thiocarbonyl*-2 : 2′-*diaminodiphenyl* was readily formed by the interaction of carbon disulphide with 2 : 2′-diaminodiphenyl.

Although the formation of seven-membered rings between the 2- and the 2′-position of diphenyl is well known [*e.g.*, diphenic anhydride from diphenic acid or from fluorenone-4-carboxylic acid (Underwood and Kochmann, *J. Amer. Chem. Soc.*, 1923, **45**, 3073), and diphenimide from phenanthraquinonemonoxime (Wegerhof, *Ber.*, 1888, **21**, 2356; *Annalen*, 1889, **252**, 16, 25)], cases of the facile formation of eight-membered rings between these positions are rare (compare Kenner and Stubbings, J., 1921, **119**, 593; Barber and Smiles, J., 1928, 1141) : presumably the rings so obtained are strainless, possibly in consequence of the diphenyl nuclei having revolved about their common axis (as in IV) to give structures having a rigidity greater than that of the *d*- and *l*-forms of the uniaxial non-coplanar diphenic acids (see *Ann. Reports*, 1927).

2 : 2′-Diacetamidodiphenyl was readily dibrominated, giving 5 : 5′-*dibromo*-2 : 2′-*diacetamidodiphenyl*. The corresponding *amine* and phenanthraquinone slowly formed a diphenylylenedibenzoctdiazine in contrast with 4 : 4′-*dibromo*-2 : 2′-*diaminodiphenyl*, which remained unaffected under the same treatment. No definite compounds were isolated from the interaction of 2 : 2′-diaminodi-

phenyl with ethyl malonate, ethyl phthalate, or ethyl oxalate (compare Le Fèvre and Turner, J., 1928, 245).

The ability of the aromatic nuclei in 2 : 2′-diaminodiphenyl to rotate about their common axis is further indicated by the complete absence of steric hindrance during *NN′*-disubstitution : *e.g.*, with the appropriate reagents, *disalicylidene*, dibenzoyl, diacetyl, and diformyl (Täuber, *Ber.*, 1891, **24**, 198) derivatives are formed *exclusively*. Similarly, 1-chloro-2 : 4-dinitrobenzene condenses with 2 : 2′-diaminodiphenyl to give mainly 2 : 2′-*di*(2″ : 4″-*dinitrophenylamino*)*diphenyl*, accompanied by some N-2′ : 4′-*dinitrophenylcarbazole*. The ready formation of α- and β-*naphthyl* and *benzyl hydrogen diphenates* from diphenic anhydride and the corresponding hydroxylic compounds further illustrates essentially the same point.

EXPERIMENTAL.

4-*Salicylideneamino*-4′-*malonylamidodiphenyl*.—A solution of " malonylbenzidine " (prepared according to Remfry, *loc. cit.*) in cold sulphuric acid gave on dilution with ice a colourless amorphous *sulphate* [Found : N, 9·5. $(C_{15}H_{12}O_2N_2)_2,H_2SO_4$ requires N, 9·3%]. A few grams of the base were boiled with an excess of a salicylaldehyde–phenol mixture and the yellowish-red solution produced was cooled. The *salicylidene* derivative crystallised from phenol in light yellow, thin plates, m.p. 298—300° (Found : N, 8·0. $C_{22}H_{16}O_3N_2$ requires N, 7·9%).

Action of Salicylaldehyde on Carbonyl- and Thiocarbonyl-dianisidines.—These substances (prepared essentially as described by Starke, *loc. cit.*), on subjection to the above treatment, slowly formed yellow insoluble powders, which were repeatedly extracted with boiling alcohol [Found : N, from 7·6 to 7·8% for the carbonyl derivative and from 7·2 to 7·5% for the thiocarbonyl derivative. $C_{22}H_{18}O_4N_2$ and $C_{22}H_{18}O_3N_2S$ require N, 7·5 and 7·2%, respectively. The more probable formulæ $(C_{21}H_{18}O_3N)\cdot NH\cdot CO\cdot NH(C_{21}H_{18}O_3N)$ and $(C_{21}H_{18}O_3N)\cdot NH\cdot CS\cdot NH(C_{21}H_{18}O_3N)$ require N, 7·8 and 7·6%, respectively].

" Oxalyl-*o*-tolidine " (Taussig, *loc. cit.*), after dissolution in boiling salicylaldehyde and precipitation by alcohol, gave a colourless powder, m. p. above 300° (Found : N, 6·9. $C_{22}H_{24}O_6N_2$ requires N, 6·8%).

Preparation of 2 : 2′-*Diaminodiphenyl*.—The addition of sand in the preparation of 2 : 2′-dinitrodiphenyl (Ullmann and Bielecki, *Ber.*, 1901, **34**, 2177) is unnecessary. To 60 g. of gently boiling *o*-chloronitrobenzene, 60 g. of copper bronze were slowly added, and the mixture was heated under a long (2 m.) air-condenser over a small flame ; reaction was complete after ½ hour. The product was thrice extracted with rectified spirit (50 c.c.) and purified in the usual manner. It was reduced with iron, water, and hydrochloric acid to 2 : 2′-diaminodiphenyl (yield, 50—60%), which was extracted from the iron paste by boiling alcohol and precipitated as sulphate.

2 : 2′-*Disalicylideneaminodiphenyl* formed long yellow needles, m. p. 153—154° (Found : N, 7·3. $C_{26}H_{20}O_2N_2$ requires N, 7·2%). The same product was formed when half the calculated weight of salicylaldehyde was used.

NN′-*Thiocarbonyl*-2 : 2′-*diaminodiphenyl*.—A mixture of diaminodiphenyl (2 g.), carbon disulphide (10 c.c.), and ethyl alcohol (50 c.c.) was boiled under reflux for 1 day. On cooling over-night, bunches of colourless needles separated, m. p. 242—243°. Recrystallisation from salicylaldehyde gave colourless flakes, m. p. 243° (Found : N, 12·5. $C_{13}H_{10}N_2S$ requires N, 12·4%).

13 : 14-(oo′-*Diphenylylene*)*dibenzoct*-12 : 15-*diazine*.—Solutions of 7·4 g. of 2 : 2′-diaminodiphenyl in 40 c.c. of hot acetic acid and of 8·3 g. of phenanthraquinone in 160 c.c. were mixed and kept at 100° for 2 hours. After 12 hours, a canary-yellow, crystalline powder (11 g.) was filtered off and recrystallised from much boiling acetic acid, the *octdiazine* being obtained in small compact crystals, m. p. 268—269° (Found : N, 8·0. $C_{26}H_{16}N_2$ requires N, 7·9%).

Repetition of the preparation of Täuber's " di-*m*-nitrodi-*o*-aminobiphenyl " (*Ber.*, 1892, **25**, 129) has always given a product which is probably a mixture of (chiefly) the 5 : 5′-, 4 : 4′, and 4 : 5′-dinitro-derivatives, together with the 3 : 3′- and 3 : 5′-compounds. Attempts to prepare dinitro-octdiazines from it were unsuccessful, as was also the condensation of 2 : 2′-diaminodiphenyl and benzil-3 : 3′-disulphonic acid (Kafka, *Ber.*, 1891, **24**, 794).

5 : 5′-*Dibromo*-2 : 2′-*diacetamidodiphenyl*.—A solution of 7 g. of 2 : 2′-diacetamidodiphenyl (prepared by Brady and McHugh's process, J., 1923, **123**, 2047, for diacetylbenzidine) in 50 c.c. of acetic acid was mixed with 9 g. of bromine in 30 c.c. of acetic acid and heated at 90—100° for 15 minutes. The *dibromo*-derivative (5 g.) obtained crystallised from slightly diluted acetic acid as a heavy, colourless, granular powder, m. p. 266—267° (Found : N, 6·7. $C_{16}H_{14}O_2N_2Br_2$ requires N, 6·5%). A further 5·8 g. were obtained from the bromination mother-liquor (total yield, about 90%).

5 : 5′-*Dibromo*-2 : 2′-*diaminodiphenyl*, prepared by refluxing the diacetyl derivative (2 g.) with 40 c.c. of 2*N*-sodium hydroxide and 30 c.c. of alcohol for 10 hours, separated on cooling and crystallised from rectified spirit in colourless needles, m. p. 140—141° (Found : N, 8·2. $C_{12}H_{10}N_2Br_2$ requires N, 8·2%).

5 : 5′-*Dibromo*-2 : 2′-*disalicylideneaminodiphenyl* formed a yellow, microcrystalline powder, sparingly soluble in the common solvents :

m. p. 263—265° (Found: N, 5·2. $C_{26}H_{18}O_2N_2Br_2$ requires N, 5·1%).

3 : 8-*Dibromo*-13 : 14-(oo'-*diphenylylene*)*dibenzoct*-12 : 15-*diazine*. —A mixture of 3·4 g. of 5 : 5'-dibromo-2 : 2'-diaminodiphenyl and 2·1 g. of phenanthraquinone was heated at 100° with 150 c.c. of acetic acid for 8 hours. The *octdiazine* obtained on cooling was sparingly soluble in the ordinary solvents but crystallised from phenol–acetic acid in small, yellow, granular crystals, m. p. above 280° (Found: N, 5·6. $C_{26}H_{14}N_2Br_2$ requires N, 5·4%).

Reduction of 4 : 4'-*Dibromo*-2 : 2'-*dinitrodiphenyl*.—A mixture of 10 g. of iron filings (previously boiled with dilute hydrochloric acid), 30 c.c. of water, and 2 g. of the dibromo-compound (prepared according to Ullmann and Bielecki, *loc. cit.*, from 2 : 5-dibromo-1-nitrobenzene) was heated at 100° for 6 hours and frequently stirred. The iron residues were separated from the diluted mixture and extracted with alcohol. A portion of the extract, after being boiled with salicylaldehyde, gave a *disalicylidene* derivative, m. p. 210—211° (Found: N, 5·2. $C_{26}H_{18}O_2N_2Br_2$ requires N, 5·1%); the remainder, when evaporated to the crystallisation point and cooled, gave the diamine as a colourless powder, m. p. 192—194°.

Interaction of 2 : 2'-*Diaminodiphenyl with* 1-*Chloro*-2 : 4-*dinitrobenzene*.—5 G. of the diamine and 15 g. of chlorodinitrobenzene were gently boiled together for 10 minutes, hydrogen chloride being evolved. The dark red reaction mixture was extracted with four lots (20 c.c.) of boiling alcohol. The extracts, on cooling, deposited light yellow plates, m. p. 163°, which crystallised from alcohol–salicylaldehyde in long yellow needles, m. p. 177—178°, of 2 : 2'-*di*-(2'' : 4''-*dinitrophenylamino*)*diphenyl* (Found: N, 16·7. $C_{24}H_{16}O_8N_6$ requires N, 16·3%). The residue from the alcoholic extraction crystallised from acetic acid in red plates, m. p. 216—217°, of N-2' : 4'-*dinitrophenylcarbazole* (Found: N, 12·7. $C_{18}H_{11}O_4N_3$ requires N, 12·6%).

Benzyl Hydrogen Diphenate.—Benzyl alcohol (10 g.) was heated at 160° for 2 hours with 20 g. of diphenic anhydride, the product dissolved in toluene, and the solution extracted with aqueous sodium carbonate. Acidification of the extract gave a gum, which was dried in benzene solution with sodium sulphate and recovered by evaporation; it solidified when cooled and scratched. The solid was sparingly soluble in the lighter petroleums and very soluble in benzene and alcohol but crystallised from 50% water–acetic acid in cubes, m. p. 112—113° (Found: C, 75·7; H, 4·9. $C_{21}H_{16}O_4$ requires C, 75·9; H, 4·8%).

α-Naphthyl Hydrogen Diphenate.—A mixture of α-naphthol (4·3 g.) and diphenic anhydride (6·7 g.) was heated at 160° for 3·5 hours.

A xylene extract of the semi-crystalline product, when shaken with sodium carbonate, gave a copious precipitate of the sodium salt in white pearly plates. This was washed with benzene, dried at room temperature, and acidified in aqueous suspension. The *naphthyl hydrogen diphenate* (8 g., m. p. 190—198°) obtained crystallised from acetic acid in long prisms, m. p. 202—203° (Found : C, 78·1 ; H, 4·4. $C_{24}H_{16}O_4$ requires C, 78·3 ; H, 4·3%).

β-*Naphthyl hydrogen diphenate*, prepared similarly, crystallised from acetic acid in small prisms, m. p. 178—179° (Found : C, 78·2 ; H, 4·3%).

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