411. *Some Derivatives of Diphenylamine and a New Synthesis of* N-*Arylanthranilic Acids and of Acridones.*

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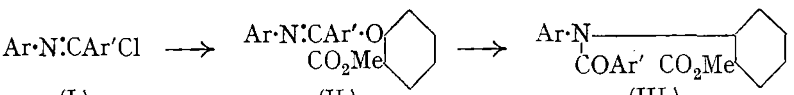
The main subject dealt with is a new synthesis of substituted diphenylamine-2-carboxylic acids, which are important because of their ready cyclisation to acridones or 5-chloroacridines, from which antimalarial drugs are derived.

DURING an extended stereochemical study of derivatives of tervalent nitrogen, we have had occasion to prepare a number of new substituted diphenylamines. By straightforward application of the convenient method of Chapman (J., 1929, 569 and previous papers) we have obtained 2 : 4'-*dichloro-*, 2 : 4 : 4'-*trichloro-*, 2 : 4 : 6 : 2' : 4'-*pentachloro-* and 4-*chloro-*4'-*bromo-diphenylamine.* These substances could not be caused to react with *p*-toluenesulphonyl chloride, even in presence of quinoline at high temperatures, and while *p*-chloro- and 2 : 4'-dichloro-diphenylamine were found to give N-*nitroso*-derivatives, under the conditions used by Fischer for nitrosating diphenylamine (*Annalen*, 1878, **190**, 175), pentachlorodiphenylamine could not be induced to react with nitrous acid or its esters in any of the circumstances which seemed likely to favour reaction. Similarly, the pentachloro-compound was indifferent to carbonyl chloride at high temperatures, whereas the trichloro-compound reacted readily with it at 140—150°. This method of preparation of 2 : 4 : 4'-*trichlorodiphenylcarbamyl chloride* has incidentally been applied to the preparation of diphenylcarbamyl chloride itself, which substance is obtainable far more readily by the new process than by those described in the literature (Erdmann and Huth, *J. pr. Chem.*, 1897, **56**, 7; D.R.-P. 285,134).

By reduction of the *N*-nitroso-derivatives of *p*-chloro- and 2 : 4'-dichloro-diphenylamine, we have prepared 4-*chloro-* and 2 : 4'-*dichloro*-NN-*diphenylhydrazine,* but the difficulty of effecting such reductions made a proposed study of the hydrazines impossible.

For another section of the investigation, we required substituted diphenylamine-carboxylic acids. Some of these acids are readily obtainable by condensing anthranilic acids with halogeno-derivatives of aromatic hydrocarbons (Goldberg and Nimerowsky, *Ber.*, 1907, **40**, 2449) or *o*-halogenobenzoic acids with aromatic bases (Ullmann, *Annalen,* 1907, **355**, 312), but of these four types only the last-named permits of much variation. We have found that the Chapman diphenylamine synthesis can be applied to the preparation of *N*-arylanthranilic acids, and the method is available also for obtaining *N*-aroyl-*N*-arylanthranilic acids, which cannot be produced by direct *N*-aroylation.

The readily accessible imino-chlorides (I) react almost quantitatively with the sodium derivatives of esters of salicylic acids, and the ethers (II) formed undergo the Chapman

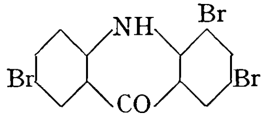


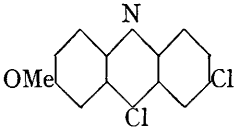
(I.) (II.) (III.)

conversion with unusual ease, to give the aroylarylanthranilic esters (III). The change (II) ⟶ (III) usually occurs at about 270°, and is markedly exothermic, the temperature rising spontaneously as much as 30°, the rise depending partly on the scale of the operation. None of Chapman's recorded changes showed this exothermic effect, which is no doubt due to the acceleration of the process by the carbalkoxy-group, Chapman having already shown (J., 1927, 1743) that the isomerisation of imino-ethers in general is promoted by the presence of an electron-attracting group in the migrating nucleus. Hydrolysis of esters of type (III) proceeds quantitatively, and in this way diphenylamine-2-carboxylic acid and its 4'-chloro-, 2' : 4'-dichloro-, 4 : 6 : 4'-*tribromo-*, 4-chloro-4'-methoxy- and 2' : 4'-*dimethyl-* derivatives have been obtained. Former syntheses would have failed in the case of the tribromo-acid, and the present synthesis thus makes possible the preparation of a number of new acridones and the corresponding 5-chloroacridines. From the tribromo-acid, 1 : 3 : 7-*tribromoacridone* (IV) has been obtained by the phosphoryl chloride method of

Drosdov (*J. Gen. Chem. Russ.*, 1934, **4**, 117). Feldman and Kopeliovitsch (*Arch. Pharm.*, 1935, **273**, 488), in studies of substances resembling "atebrin," prepared **3** : 5-dichloro-7-methoxyacridine (V) from 4-chloro-4′-methoxydiphenylamine-2-carboxylic acid, but their synthesis, of the Ullmann type, necessitates the use of the difficultly accessible 2 : 5-dichlorobenzoic acid.

(IV.)

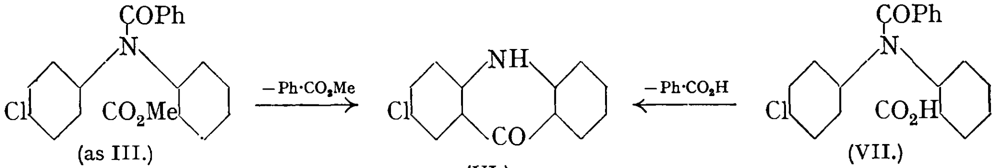




(V.)

All the *N*-arylanthranilic acids obtained by the new method are free from the impurities which appear to be unavoidable in the products of the older syntheses.

Some methyl esters of type (III) (Ar′ = Ph) lose methyl benzoate when heated and pass into the corresponding acridones (VI), although not quantitatively. The one *l*-menthyl ester examined gave *l*-menthene, benzoic acid and the acridone.



(as III.) (VI.) (VII.)

Partial hydrolysis of the esters (III) is readily effected. Some of the *N*-aroyl-*N*-arylanthranilic acids (VII) so obtained lose benzoic acid when they are heated for a few minutes and again an acridone is formed. This is actually one of the most expeditious methods of obtaining an acridone, as the yields are good and the product is easily purified. Curiously enough, *N*-benzoyl-*N*-phenylanthranilic acid does not undergo this conversion into acridone at temperatures up to 350°.

Substituted diphenylamine-4-carboxylic acids are readily obtained from *p*-hydroxybenzoic esters.

EXPERIMENTAL.

Preparation of Halogenodiphenylamines.—The experimental procedure described by Chapman (*loc. cit.*) was followed without modification.

N-o-*Chlorophenylbenzimino*-p-*chlorophenyl ether*, large irregular crystals from alcohol, has m. p. 59—60° (Found : Cl, 20·9. $C_{19}H_{13}ONCl_2$ requires Cl, 20·8%). Yield, 90%.

N-*Benzoyl*-2 : 4′-*dichlorodiphenylamine* was formed in 74% yield when the last-named compound was heated at 300° for 2 hours. It crystallised from alcohol in prisms, m. p. 115° (Found : Cl, 20·8. $C_{19}H_{13}ONCl_2$ requires Cl, 20·8%).

2 : 4′-*Dichlorodiphenylamine*, large prisms from alcohol, has m. p. 42° (Found : Cl, 30·3. $C_{12}H_9NCl_2$ requires Cl, 29·8%). Yield, 71%.

N-2 : 4-*Dichlorophenylbenzimino*-p-*chlorophenyl ether* crystallised from alcohol in hexagonal plates, m. p. 81° (Found : Cl, 28·1. $C_{19}H_{12}ONCl_3$ requires Cl, 28·3%). Yield, 96%.

N-*Benzoyl*-2 : 4 : 4′-*trichlorodiphenylamine*, formed in 76% yield by heating the preceding ether for 2 hours at 250—270°, separated from light petroleum (b. p. 80—100°) in rhombs, m. p. 117—118° (Found : Cl, 28·5. $C_{19}H_{12}ONCl_3$ requires Cl, 28·3%).

2 : 4 : 4′-*Trichlorodiphenylamine* crystallised from light petroleum (b. p. 60—80°) in angular plates, m. p. 67—68° (Found : Cl, 39·1. $C_{12}H_8NCl_3$ requires Cl, 39·3%). Yield, 85%.

N-*p*-Chlorophenyl-*p*-toluimino-2 : 4-dichlorophenyl ether, $C_6H_4Cl\cdot N{:}C(C_6H_4Me)\cdot O\cdot C_6H_3Cl_2$, was prepared from 2 : 4-dichlorophenol and *N*-*p*-chlorophenyl-*p*-toluanilideiminochloride, the latter being obtained by the action of phosphorus pentachloride on *p*-tolu-*p*-chloroanilide. The ether was an uncrystallisable glass.

N-p-*Toluoyl*-2 : 4 : 4′-*trichlorodiphenylamine* was obtained by heating the above glass for 2·5 hours at 280—300°. The black glass which resulted was crystallised from light petroleum (b. p. 80—100°), then twice from alcohol, and finally from glacial acetic acid. The p-*toluoyl* derivative formed irregular prisms, m. p. 157° (Found : Cl, 27·2. $C_{20}H_{14}ONCl_3$ requires Cl, 27·3%).

N-p-*Chlorophenylbenzimino*-2′-(*carbo*-l-*menthoxy*)*phenyl ether* was obtained as an uncrystallisable glass (yield, 88%) from benz-*p*-chloroanilideiminochloride and *l*-menthyl salicylate. When heated at 280—295°, it passed into *N*-benzoyl-4-chloro-2′-(carbo-*l*-menthoxy)diphenylamine, but this at once began to decompose, giving (1) *l*-menthene, b. p. 165°, (2) benzoic acid, and (3) 3-chloroacridone.

N-2 : 4-*Dichlorophenylbenzimino*-2 : 4 : 6-*trichlorophenyl ether* separated from alcohol in prisms, m. p. 86—88° (Found: Cl, 39·9. $C_{19}H_{10}ONCl_5$ requires Cl, 39·8%). Yield, 88%.

N-*Benzoyl*-2 : 4 : 6 : 2′ : 4′-*pentachlorodiphenylamine*, formed in 81% yield by heating the preceding ether for 2 hours at 250—270°, crystallised from alcohol in prisms, m. p. 160° (Found: Cl, 39·6. $C_{19}H_{10}ONCl_5$ requires Cl, 39·8%).

2 : 4 : 6 : 2′ : 4′-*Pentachlorodiphenylamine* crystallised from alcohol in slender needles, m. p. 94° (Found: Cl, 51·6. $C_{12}H_6NCl_5$ requires Cl, 51·9%). Yield, 92%. The *N*-nitroso-derivative could not be obtained by using (*a*) sodium nitrite and hydrochloric acid in alcoholic solution, (*b*) amyl nitrite and hydrochloric acid in glacial acetic acid solution, (*c*) sodium nitrite and concentrated sulphuric acid.

N-p-*Bromophenylbenzimino*-p-*chlorophenyl ether* separated from alcohol in prisms, m. p. 83—84° (0·1698 gave 0·1449 AgCl + AgBr. $C_{19}H_{13}ONClBr$ requires 0·1449 AgCl + AgBr).

N-*Benzoyl*-4-*chloro*-4′-*bromodiphenylamine*, obtained in 75% yield by heating the last-named ether for 2·5 hours at 290—320°, crystallised from alcohol in plates, m. p. 149° (0·1424 gave 0·1194 AgCl + AgBr. $C_{19}H_{13}ONClBr$ requires 0·1249 AgCl + AgBr).

4-*Chloro*-4′-*bromodiphenylamine* formed plates, m. p. 91·5°, from alcohol (0·1272 gave 0·1477 AgCl + AgBr. $C_{12}H_9NClBr$ requires 0·1489 AgCl + AgBr).

N-*Nitroso*-p-*chlorodiphenylamine* crystallised from light petroleum (b. p. 40—60°) in prisms, m. p. 88° (Found: Cl, 15·0. $C_{12}H_9ON_2Cl$ requires Cl, 15·3%). Yield, 83%.

N-*Phenyl*-N-p-*chlorophenylhydrazine*, prepared by reducing the above nitroso-compound with zinc dust and aqueous alcoholic acetic acid by the Fischer method (*loc. cit.*), contained a high proportion of *p*-chlorodiphenylamine, which survived the usual hydrochloride separation. By crystallising the acid oxalate this difficulty was avoided, and the *hydrazine* was obtained as a pale golden oil, b. p. 194°/2 mm. (Found: Cl, 16·1. $C_{12}H_{11}N_2Cl$ requires Cl, 16·2%).

N-*Nitroso*-2 : 4′-*dichlorodiphenylamine* formed yellow needles, m. p. 66—67°, from light petroleum (b. p. 60—80°) (Found: Cl, 26·6. $C_{12}H_8ON_2Cl_2$ requires Cl, 26·6%). Yield, 82%.

2 : 4′-*Dichloro*-NN-*diphenylhydrazine*.—The preceding nitroso-compound was reduced with zinc dust and aqueous alcoholic acetic acid. The resulting paste was extracted with alcohol. The extract was treated with concentrated hydrochloric acid. The crystalline material precipitated was shaken with a mixture of water and light petroleum, whereupon dichlorodiphenylamine passed into the latter and the aqueous layer yielded almost pure *dichlorodiphenylhydrazine*. This was a pale yellow oil, b. p. 241°/8 mm. (Found: Cl, 28·9. $C_{12}H_{10}N_2Cl_2$ requires Cl, 28·1%). Yield, 25%.

N-2-*Chlorophenyl*-N-4-*chlorophenyl*-N′N′-4-*chlorophthalylhydrazine*,

$N(C_6H_4Cl)(C_6H_4Cl){\cdot}N{:}C_2O_2{:}C_6H_3Cl$.

—Equimolecular quantities of 2 : 4′-dichlorodiphenylhydrazine and 4-chlorophthalic anhydride were heated at 170—190° for an hour. Alcohol was added, the mixture boiled for an hour, the alcohol evaporated, and the residual powder ground with dilute sodium carbonate solution. The *chlorophthalyl* derivative left crystallised from alcohol in yellow clusters of needles, m. p. 142—142·5° (Found: Cl, 25·2. $C_{20}H_{11}O_2N_2Cl_3$ requires Cl, 25·5%).

2 : 4 : 4′-*Trichlorodiphenylcarbamyl Chloride*.—Carbonyl chloride was bubbled through 10 g. of 2 : 4 : 4′-trichlorodiphenylamine at 150—200° until no further increase in weight occurred (about 30 minutes). When the cooled product was crystallised from alcohol, the *chloride* was obtained in needles, m. p. 117—118° (Found: Cl, 42·3. $C_{13}H_7ONCl_4$ requires Cl, 42·4%). Yield, 68%.

Diphenylcarbamyl chloride was obtained similarly (temperature, 140—150°; 15 minutes; yield, 92%).

N-p-*Chlorophenylbenzimino*-o-*carbomethoxyphenyl Ether*.—To a cooled solution of sodium (14·5 g.; 1·25 atoms) in 700 c.c. of absolute alcohol were added in rapid succession (1) 114 g. (1·5 mols.) of methyl salicylate and (2) 130 g. (1 mol.) of benz-*p*-chloroanilideiminochloride, dissolved in dry ether. The mixture became cloudy, and was kept overnight. The ether and most of the alcohol were then removed by evaporation, and water added. The *ether* became solid; it crystallised from alcohol in angular plates, m. p. 130—131° (Found: Cl, 9·9. $C_{21}H_{16}O_3NCl$ requires Cl, 9·7%). Yield, 166 g. (88%).

Methyl N-*Benzoyl*-4-*chlorodiphenylamine*-2′-*carboxylate*.—The above imino-ether (30 g.)

was heated in a wide tube in a bath kept at 270—2. As soon as the temperature inside the tube attained that of the bath, isomeric change began, and the internal temperature rose to about 300° within a few minutes. When it began to fall, the product was poured into alcohol (2 vols.). On cooling, the *methyl* ester separated in prisms, m. p. 139—140° (Found : Cl, 9·5. $C_{21}H_{16}O_3NCl$ requires Cl, 9·7%). Yield of pure substance, 85—91%.

When the ester was heated at 320°, methyl benzoate (b. p. 199°) distilled, and 3-chloroacridone was formed. The latter crystallised from *cyclo*hexanol in yellow needles, m. p. above 360° (compare Ullmann, *loc. cit.*) (Found : Cl, 15·4. Calc. : Cl, 15·4%).

N-*Benzoyl*-4-*chlorodiphenylamine*-2′-*carboxylic Acid.*—For this, and similar partial hydrolyses of esters of *N*-benzoyl derivatives, it was convenient to have ready a solution (*S*) made by dissolving 2·3 g. of sodium in 100 c.c. of absolute alcohol, and adding 20 c.c. of water. A solution containing the methyl ester (11 g.; 1 mol.), 60 c.c. of absolute alcohol, 33 c.c. of solution *S* (equivalent to 1 atom of sodium), and 33 c.c. of water was boiled under reflux for an hour. The alcohol was evaporated, and the residue acidified with hydrochloric acid. The precipitate was extracted with sodium hydrogen carbonate solution, and the filtered extract acidified. The precipitate was freed from benzoic acid by extraction with boiling water, dried, and crystallised from acetone–light petroleum (b. p. 40—60°). It formed needles, m. p. 191—192° (Found : Cl, 10·2. $C_{20}H_{14}O_3NCl$ requires Cl, 10·1%). Yield, 8 g. (76%).

Action of Heat on the Preceding Acid.—The acid was heated rapidly to 250° during 5 minutes. The resulting mixture was freed from benzoic acid by extraction with boiling water, and 3-chloroacridone obtained in 90% yield.

4-*Chlorodiphenylamine*-2′-*carboxylic Acid.*—A solution of methyl *N*-benzoyl-4-chlorodiphenylamine-2′-carboxylate (10 g.) in 125 c.c. of alcohol was treated with 40 g. of sodium hydroxide in 40 c.c. of water, and the whole then boiled under reflux for an hour. The alcohol was evaporated, and the aqueous solution acidified with hydrochloric acid. The precipitate was freed from benzoic acid by extraction with boiling water; the residual carboxylic acid crystallised from alcohol in pale yellow prisms, m. p. 177—178° (Ullmann, *loc. cit.*, gives 177°; the product obtained by the Ullmann method was less easily purified). Yield, almost theoretical. The acid was readily converted into 3-chloroacridone by Drosdov's method (*loc. cit.*). Yield, 87%.

N-2 : 4-*Dichlorophenylbenzimino*-o-*carbomethoxyphenyl ether*, obtained from benz-2 : 4-dichloroanilideiminochloride and methyl salicylate in 72% yield, crystallised from alcohol in needles, m. p. 85—87° (Found : Cl, 17·6. $C_{21}H_{15}O_3NCl_2$ requires Cl, 17·7%).

Methyl N-*benzoyl*-2 : 4-*dichlorodiphenylamine*-2′-*carboxylate* was obtained in 65% yield by heating the last-named ether at 260—280° for 10 minutes. It formed rods, m. p. 114—116°, from ethyl alcohol (Found : Cl, 17·6. $C_{21}H_{15}O_3NCl_2$ requires Cl, 17·7%).

N-*Benzoyl*-2 : 4-*dichlorodiphenylamine*-2′-*carboxylic acid* was obtained by partial hydrolysis of the benzoyl-methyl ester. After being dissolved in sodium bicarbonate solution and precipitated therefrom with acid, it was hydrated, and therefore was dried in a high vacuum over phosphoric oxide (Found : Cl, 18·5. $C_{20}H_{13}O_3NCl_2$ requires Cl, 18·4%). The acid crystallised from benzene or from light petroleum–acetone in needles, solvated in both cases. The product from the second solvent had m. p. 177°.

2′ : 4′-*Dichlorodiphenylamine*-2-*carboxylic Acid.*—The benzoyl ester was hydrolysed with excess of alcoholic sodium hydroxide. The crude acid obtained (93% yield) had m. p. 243° (Ullmann, *loc. cit.*, gave 249° for the pure acid).

4-m-*Xylylbenzimino*-2′-*carbomethoxyphenyl ether*, formed from benz-4-*m*-xylidideiminochloride in 56% yield, crystallised from alcohol in rectangular prisms, m. p. 87—88° (Found : C, 76·7; H, 6·0. $C_{23}H_{21}O_3N$ requires C, 76·85; H, 5·9%).

Methyl N-*benzoyl*-2 : 4-*dimethyldiphenylamine*-2′-*carboxylate* was formed in 89% yield by heating the preceding ether at 275° for 10 minutes, and crystallised from methyl alcohol in stout prisms, m. p. 132—133° (Found : C, 76·7; H, 5·7. $C_{23}H_{21}O_3N$ requires C, 76·85; H, 5·9%). The ester showed no tendency to give the corresponding acridone when heated at 350°.

N-*Benzoyl*-2 : 4-*dimethyldiphenylamine*-2′-*carboxylic acid*, obtained by hydrolysing the methyl ester, crystallised from acetone–light petroleum (b. p. 40—60°) in prisms, softening at 191°, and melting at 192—193° (Found : C, 76·4; H, 5·6. $C_{22}H_{19}O_3N$ requires C, 76·5; H, 5·7%). Yield, 74%.

Action of Heat on the Preceding Acid.—The acid was heated for a few minutes at 300°. The residue was extracted with boiling alcohol, 1 : 3-dimethylacridone being left as small yellow needles, m. p. 307°. Yield, 71%.

N-*Phenylbenzimino*-o-*carbomethoxyphenyl ether*, obtained from benzanilideiminochloride and methyl salicylate in 81% yield [illegible]d rhombohedra, m. p. 110—111°, from alcohol (Found: C, 76·2; H, 5·1. $C_{21}H_{17}O_3N$ requires C, 76·1; H, 5·2%).

Methyl N-*benzoyldiphenylamine-2-carboxylate* was formed in 73% yield by heating the last-named ether at 270—275° for 10 minutes. It crystallised from alcohol in diamond-shaped prisms, m. p. 132—133° (Found: C, 75·9; H, 4·9. $C_{21}H_{17}O_3N$ requires C, 76·1; H, 5·2%). Hydrolysis of the ester with excess of alcoholic alkali gave *N*-phenylanthranilic acid in 96% yield.

N-*Benzoyl*-N-*phenylanthranilic* [N-*benzoyldiphenylamine-2-carboxylic*] *acid*, obtained from its methyl ester in 76% yield, was crystallised from acetone–light petroleum (b. p. 40—60°) and then from benzene. It formed slender needles, m. p. 186° (Found: C, 75·7; H, 5·0. $C_{20}H_{15}O_3N$ requires C, 75·7; H, 4·8%).

N-p-*Bromophenylbenzimino-4′ : 6′-dibromo-2′-carbomethoxyphenyl Ether.*—Sodium (3·7 g.; 1·25 atoms) was dissolved in 150 c.c. of absolute alcohol, and a suspension of 50 g. (1·5 mols.) of methyl 3 : 5-dibromosalicylate in 100 c.c. of alcohol added, followed by a solution of 47 g. of benz-*p*-bromoanilideiminochloride in dry ether. The mixture was shaken for a few minutes and left overnight. Most of the solvents were removed by evaporation, and the white oil extracted with warm water until it became a solid. This crystallised from alcohol in long prisms, m. p. 105° (Found: Br, 42·8. $C_{21}H_{14}O_3NBr_3$ requires Br, 42·2%). Yield, 65%.

Methyl N-*benzoyl-4 : 6 : 4′-tribromodiphenylamine-2-carboxylate*, obtained in 87% yield by heating the preceding ether at 270°, formed small prisms, m. p. 138—139°, from alcohol (Found: Br, 42·8. $C_{21}H_{14}O_3NBr_3$ requires Br, 42·2%).

N-*Benzoyl-4 : 6 : 4′-tribromodiphenylamine-2-carboxylic acid*, obtained from its methyl ester, crystallised from acetone–light petroleum (b. p. 40—60°) in slender prisms, m. p. 217—218° (with previous softening) (Found: Br, 42·6. $C_{20}H_{12}ONBr_3$ requires Br, 43·3%).

4 : 6 : 4′-*Tribromodiphenylamine-2-carboxylic acid*, obtained from the *N*-benzoyl ester in 90% yield, crystallised from alcohol in sulphur-yellow needles, m. p. 222° (Found: Br, 52·05, 52·05. $C_{13}H_8O_2NBr_3$ requires Br, 53·3%).

1 : 3 : 7-*Tribromoacridone.*—A solution of 4 g. of the last-named acid in 80 c.c. of xylene was treated with 2 g. of phosphoryl chloride, dissolved in 20 c.c. of xylene. The whole was boiled for 2 hours. Solid slowly separated. Water and then dilute alkali were added, and the xylene was removed in a current of steam. The liquid was filtered, and the crude *tribromoacridone* dried (3·5 g.). It crystallised from *m*-cresol in minute yellow needles, m. p. above 300° (Found: Br, 54·7. $C_{13}H_6ONBr_3$ requires Br, 55·5%).

N-p-*Methoxyphenylbenzimino*-p-*chloro*-o-*carbomethoxyphenyl ether*,

$$OMe{\cdot}C_6H_4{\cdot}N{:}CPh{\cdot}O{\cdot}C_6H_3Cl{\cdot}CO_2Me,$$

from benz-*p*-anisidideiminochloride and methyl 5-chlorosalicylate, crystallised from alcohol in flat needles, m. p. 105—106° (Found: Cl, 8·7. $C_{22}H_{18}O_4NCl$ requires Cl, 9·0%).

Methyl N-*benzoyl-4-chloro-4′-methoxydiphenylamine-2-carboxylate* was obtained by heating the last-named ether at 200—210° for 10 minutes and then pouring the product into one volume of alcohol. On cooling, 7·5 g. of solid separated, and this on recrystallisation from alcohol gave the methyl ester in prisms and cubes, m. p. 164° (Found: Cl, 9·3. $C_{22}H_{18}O_4NCl$ requires Cl, 9·0%). Complete hydrolysis of the ester gave 4-chloro-4′-methoxydiphenylamine-2-carboxylic acid, m. p. 191—192° (Feldman and Kopeliovitsch, *loc. cit.*, give 185—186°).

N-*Benzoyl-4-chloro-4′-methoxydiphenylamine-2-carboxylic acid*, obtained by the partial hydrolysis of the methyl ester, crystallised from benzene, in which it was only moderately soluble, in slender needles, containing half a molecule of benzene of crystallisation, after being air-dried (Found: Cl, 8·3. $C_{21}H_{16}O_4NCl,1/2C_6H_6$ requires Cl, 8·4%). It softened and lost benzene at 120—125°, but gave no sharp m. p. at higher temperatures. The solvent-free acid was obtained from the solvated specimen by dissolution in very dilute alkali solution (the sodium salt is sparingly soluble), precipitation with dilute acid, and dehydration in a high vacuum over phosphoric oxide (Found: Cl, 9·1. $C_{21}H_{16}O_4NCl$ requires Cl, 9·3%).

Action of Heat on the Preceding Acid.—The acid was heated for 15 minutes at 300°. Benzoic acid sublimed. The mixture was extracted with boiling alcohol and the residual 3-*chloro*-7-*methoxyacridone* (yield, almost theoretical) was crystallised from phenol, to which a little alcohol was added before the solvent solidified. The acridone formed thin yellow hexagonal plates melting above 300° (Found: Cl, 13·1. $C_{14}H_{10}O_2NCl$ requires Cl, 13·7%).

N-p-*Chlorophenylbenzimino*-p′-*carbomethoxyphenyl ether* was obtained from benz-*p*-chloroanilideiminochloride and methyl *p*-hydroxybenzoate in 57% yield (pure). It crystallised from methyl alcohol in prisms, m. p. 78—79° (Found: Cl, 9·4. $C_{21}H_{16}O_3NCl$ requires Cl, 9·7%).

Methyl N-*benzoyl-4-chlorodiphenylamine-4′-carboxylate* was obtained by heating the above ether. With the bath at 277° the temperature of the mixture rose to 290°. The ester crystallised from alcohol in prisms, m. p. 140—141° (Found : Cl, 9·4. $C_{21}H_{16}O_3NCl$ requires Cl, 9·7%). Yield, 90%.

N-*Benzoyl*-4-*chlorodiphenylamine*-4′-*carboxylic acid*, obtained in 61% yield by the partial hydrolysis of the methyl-benzoyl ester, crystallised from alcohol in slender needles, m. p. 223—224° (Found : Cl, 10·1. $C_{20}H_{14}O_3NCl$ requires Cl, 10·1%).

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