301. *Internuclear Cyclisation. Part XIII.* The Decomposition of Diazonium Salts prepared from* N-o-*Aminobenzoyldiphenylamines. A New Molecular Rearrangement.*

By D. H. Hey and T. M. Moynehan.

Thermal decomposition of an aqueous solution of the diazonium chloride from *N*-*o*-aminobenzoyldiphenylamine gives 10-phenylphenanthridone and *N*-*o*-hydroxybenzoyldiphenylamine, but catalytic decomposition at room temperature by the addition of copper powder gives 10-phenylphenanthridone and diphenyl-2-carboxyanilide. Evidence on the nature of the anilide-forming rearrangement is provided by the study of similar reactions with the *N*-*o*-aminobenzoyl derivatives of di-*p*-tolylamine, 4-methyldiphenylamine, and 4-chlorodiphenylamine. The rearrangement occurs only in the catalytic decomposition of the diazonium salt.

As part of a study of the Pschorr and related reactions the decomposition of diazonium salts from *N*-*o*-aminobenzoyldiphenylamines (I) was studied. Unsymmetrically substituted compounds of this type (*i.e.*, $R \neq R'$) can cyclise with either aromatic ring attached to the nitrogen atom; the products should provide useful evidence of the effect of substituent atoms or groups in one or both of these rings on the ring-closure.

N-*o*-Aminobenzoyldiphenylamine (I; $R = R' = H$) was obtained by reduction of *N*-*o*-nitrobenzoyldiphenylamine, prepared from *o*-nitrobenzoyl chloride and diphenylamine. When its diazonium chloride was decomposed by heating the aqueous solution, the products were 10-phenylphenanthridone (II; $R = R' = H$) and *N*-*o*-hydroxybenzoyldiphenylamine. The identity of the former was at first in question because it had m. p. 225°, whereas Walls[1] had claimed to have prepared this compound by heating 9-bromophenanthridine with phenol and had recorded m. p. 118—119°. It seemed possible that Walls's compound might be 9-phenoxyphenanthridine (V; $R = H$) and this was confirmed when it was found that the compound of m. p. 118—119°, on being heated at 360°,

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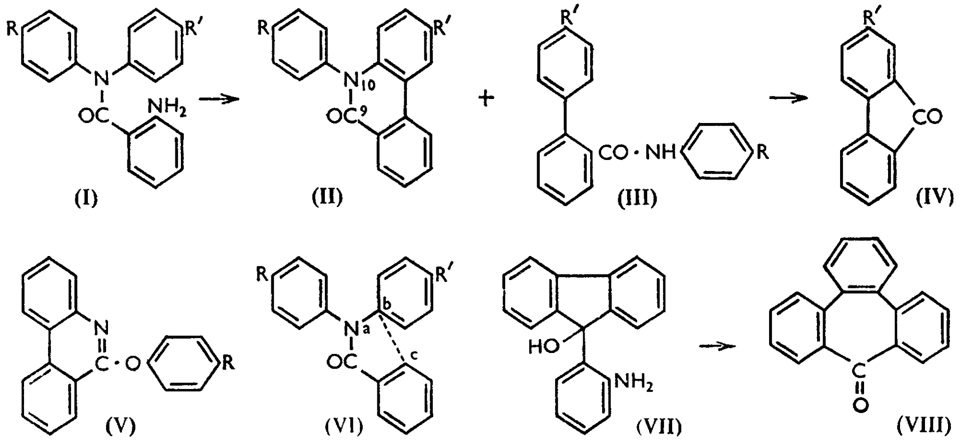
* Part XII, *J.*, **1957**, 1781.

[1] Walls, *J.*, **1934**, 104.

rearranged to a compound, m. p. 225°, identical with our product. This rearrangement is analogous to Chapman's synthesis of diphenylamine [2] in which phenyl *N*-phenylbenzimidate is converted by heat into *N*-benzoyldiphenylamine. When, however, the aqueous diazonium chloride prepared from *N*-*o*-aminobenzoyldiphenylamine was decomposed at room temperature by addition of copper powder, the product consisted of 10-phenylphenanthridone and diphenyl-2-carboxyanilide (III; R = R′ = H). The constitution of the latter was confirmed by its identity with an authentic specimen and by conversion into fluorenone after being heated with phosphoric acid. A similar result was obtained when the diazonium fluoroborate from *N*-*o*-aminobenzoyldiphenylamine was decomposed in acetone by addition of copper powder.

The unexpected formation of the anilide (III) is clearly due to a new type of molecular rearrangement in which an aryl group migrates from the nitrogen atom to the nuclear position to which the diazonium group was originally attached. There are two possible routes for such a rearrangement. The nuclear position from which the diazonium group has been eliminated (VI, c) can become attached either to the *ortho*-position of one of the *N*-phenyl groups, followed by fission of the C–N bond (ab), or to one of the *N*-phenyl groups at the position of attachment of the nitrogen atom, again followed by fission of the C–N bond (as in VI). A decision was made by carrying out the reaction with *N*-*o*-aminobenzoyldi-*p*-tolylamine (I; R = R′ = Me), prepared from di-*p*-tolylamine and *o*-nitrobenzoyl chloride, and subsequent reduction. Decomposition of the diazonium chloride with copper powder in aqueous solution gave 3-methyl-10-*p*-tolylphenanthridone (II; R = R′ = Me) and 4-methyldiphenyl-2′-carboxy-*p*-toluidide (III; R = R′ = Me), identical with an authentic specimen. The formation of this toluidide proves that the second route (VI) has been followed; the alternative would give a toluidide of 3-methyldiphenyl-2′-carboxylic acid.

When the diazonium fluoroborate from *N*-*o*-aminobenzoyldi-*p*-tolylamine was decomposed in acetone by copper powder a product was obtained which did not yield to separation by chromatography. On being heated with phosphoric acid, however, the product gave 3-methyl-10-*p*-tolylphenanthridone (II; R = R′ = Me) (which is not affected by this treatment) and 2-methylfluorenone (IV; R′ = Me), which must have been derived from 4-methyldiphenyl-2′-carboxy-*p*-toluidide (III; R = R′ = Me). When an aqueous solution of the diazonium chloride from *N*-*o*-aminobenzoyldi-*p*-tolylamine was heated (without copper powder) an intractable mixture was obtained which, when treated with hot phosphoric acid, gave only 3-methyl-10-*p*-tolylphenanthridone. No 2-methylfluorenone



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[2] Chapman, *J.*, 1927, 1743.

was formed, and therefore under these conditions no rearrangement can have occurred. Authentic specimens of both 3- and 4-methyldiphenyl-2′-carboxy-*p*-toluidide were prepared from the appropriate iodotoluene and methyl *o*-iodobenzoate by an Ullmann reaction, followed by hydrolysis to the acid and thence to the *p*-toluidide.

The rearrangement described above bears a superficial resemblance to another reported by Stiles and Libbey,[3] to which brief reference has been made elsewhere.[4] These authors reported that the decomposition of the diazonium sulphate from 9-*o*-aminophenyl-9-fluorenol (VII) gave, in addition to the phenol, tribenzotropone (VIII) in 24% yield.

In both this rearrangement and the one now reported the nuclear position from which the nitrogen is eliminated attacks a second nucleus at the point of attachment of an extranuclear carbon or nitrogen atom with subsequent fission of a carbon–carbon or carbon–nitrogen bond respectively. The two rearrangements, however, differ in that Stiles and Libbey's proceeds on warming the aqueous diazonium solution, whereas ours only proceeds in the cold by addition of copper powder.

With an unsymmetrically substituted *o*-aminobenzoyldiphenylamine (*e.g.*, I; $R \neq R'$) the decomposition of the diazonium chloride could in the absence of copper powder give a mixture of two isomeric 10-arylphenanthridones, and in the presence of copper powder a mixture of two isomeric diphenyl-2-carboxyanilides in addition. In order to test to what extent these possibilities are realised, reactions have been carried out with *N*-*o*-aminobenzoyl-4-methyldiphenylamine (I; R = Me, R′ = H) and *N*-*o*-aminobenzoyl-4-chlorodiphenylamine (I; R = Cl, R′ = H). 4-Methyl- and 4-chloro-diphenylamine, prepared from benz-*p*-toluidide and benz-*p*-chloroanilide respectively by Chapman's method,[2] were converted into the *o*-aminobenzoyl derivatives. With both of these monosubstituted *N*-*o*-aminobenzoyldiphenylamines, the thermal decomposition of the diazonium salts in aqueous solution gave only phenanthridones, but the decomposition at room temperature in the presence of copper powder gave mixtures of phenanthridones and diphenyl-2′-carboxyanilides. Treatment of these mixtures with hot phosphoric acid converted the anilides into fluorenones. The mixtures of fluorenones thus obtained could not be separated but were analysed spectrophotometrically by Dewar and Urch's method.[5] In order to distinguish between the two pairs of 10-arylphenanthridones formed one member of each pair was synthesised by treating 9-chlorophenanthridine with *p*-cresol and isomerising the *p*-tolyloxyphenanthridine (V; R = Me) produced, by heat, to 10-*p*-tolylphenanthridone (II; R = Me; R′ = H); and similarly 10-*p*-chlorophenylphenanthridone (II; R = Cl; R′ = H) from 9-*p*-chlorophenoxyphenanthridine (V; R = Cl).

In order to express the ratios in which the isomeric anilides are formed in terms of the observed ratios of the fluorenones based on spectrophotometry, it was necessary to determine in what yields the anilides were converted into the fluorenones under our conditions. The four anilides concerned [diphenyl-2-carboxy-*p*-toluidide (III; R = Me; R′ = H), 4-methyldiphenyl-2′-carboxyanilide (III; R = H; R′ = Me), diphenyl-2-carboxy-*p*-chloroanilide (III; R = Cl; R′ = H), and 4-chlorodiphenyl-2′-carboxyanilide (III; R = H; R′ = Cl)] were prepared and under the standard treatment with hot phosphoric acid gave the appropriate fluorenones in yields of 96·8%, 95%, 97·2%, and 98% respectively. These values were used in calculating the yields of the anilides formed in the reactions with the monosubstituted *o*-aminobenzoyldiphenylamines.

In the thermal and catalytic decomposition of the diazonium chloride from *N*-*o*-aminobenzoyl-4-methyldiphenylamine (I; R = Me; R′ = H) only one phenanthridone was isolated. With *N*-*o*-aminobenzoyl-4-chlorodiphenylamine the catalytic decomposition gave the two phenanthridones in approximately equal amounts, whereas in the thermal decomposition the major product was 10-*p*-chlorophenylphenanthridone (II; R = Cl; R′ = H). This result is in agreement with the representation of the catalytic reaction

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[3] Stiles and Libbey, *J. Org. Chem.*, 1957, **22**, 1243.
[4] Hey and Moynehan, *Proc. Chem. Soc.*, 1957, 209.
[5] Dewar and Urch, *J.*, 1957, 345.

as a homolytic process, whereas in the thermal decomposition the deactivation of the nucleus containing the chlorine atom indicates a heterolysis. With none of the four amines did thermal decomposition of an aqueous solution of the diazonium salt give any product of rearrangement, whereas in all four cases the catalysed reaction produced the rearrangement. The analyses of the mixtures of fluorenones obtained from the anilides showed that the presence of substituents has no marked effect upon this reaction, which result may be taken as indicative of a homolytic mechanism for the rearrangement (cf. de Tar[6]). Attempts to prepare 4-methoxycarbonyl-*N*-*o*-nitrobenzoyldiphenylamine, for a similar sequence of reactions with a methoxycarbonyl substituent, were unsuccessful.

The yields of the products obtained in the reactions investigated are tabulated.

Base	Method *	Phenanthridone		Anilide	
N-*o*-Aminobenzoyldiphenylamine	*A* i	10-Phenyl-	(62%)	—	
,,	*B*	,,	(40%)	Diphenyl-2-carboxyanilide	(45%)
,,	*C*	,,	(33·5%)	,,	(18·5%)
N-*o*-Aminobenzoyldi-*p*-tolylamine	*A* i	3-Methyl-10-*p*-tolyl-	(22%)	—	
,,	*B*	,,	(28%)	4-Methyldiphenyl-2′-carboxy-*p*-toluidide	(58%)
,,	*C*	,,	(31·5%)	,,	(36%) †
N-*o*-Aminobenzoyl-4-methyldiphenylamine	*A* i	10-*p*-Tolyl-	(9%)	—	
,,	*B*	,,	(14·5%)	4-Methyldiphenyl-2′-carboxyanilide	(28·4%) †
				Diphenyl-2-carboxy-*p*-toluidide	(25·2%) †
N-*o*-Aminobenzoyl-4-chlorodiphenylamine	*A* ii	10-*p*-Chlorophenyl-	(24%)	—	
		3-Chloro-10-phenyl-	(12%)		
,,	*B*	10-*p*-Chlorophenyl-	(17%)	4-Chlorodiphenyl-2′-carboxyanilide	(19%) †
		3-Chloro-10-phenyl-	(19%)	Diphenyl-2-carboxy-*p*-chloroanilide	(21%) †

* *A*, Action of heat on aqueous diazonium (i) chloride, (ii) sulphate. *B*, Action of copper powder on aqueous diazonium chloride or *C*, on diazonium fluoroborate in acetone.

† Yield calculated by conversion into corresponding fluorenone.

EXPERIMENTAL

Unless otherwise stated, light petroleum had b. p. 60—80°.

N-o-*Aminobenzoyldiphenylamine*.—Ethereal *o*-nitrobenzoyl chloride (6 g. in 20 ml.) was added slowly to diphenylamine (6 g.) in pyridine (15 ml.) and dry ether (50 ml.), and the mixture bolied under reflux for 1 hr. After removal of the ether, water was added, and recrystallisation from ethanol (charcoal) of the brown solid which separated gave N-o-*nitrobenzoyldiphenylamine* (10·3 g.), pale green plates, m. p. 158—159° (Found: C, 72·3; H, 4·3. $C_{19}H_{14}O_3N_2$ requires C, 71·7; H, 4·4%). A solution of this (8 g.) in benzene (150 ml.) with Raney nickel (8 g.) was hydrogenated at room temperature and pressure. The catalyst was filtered off and the solution concentrated. Recrystallisation of the residual white solid from benzene gave N-o-*aminobenzoyldiphenylamine* (6·4 g.) in needles, m. p. 178—179° (Found: C, 79·8; H, 5·5. $C_{19}H_{16}ON_2$ requires C, 79·2; H, 5·6%).

Thermal Decomposition in Aqueous Solution of the Diazonium Chloride from N-o-*Aminobenzoyldiphenylamine*.—The amine (3·5 g.), suspended in concentrated hydrochloric acid (20 ml.) and water (40 ml.), was diazotised at 0° with sodium nitrite (1 g.) in water (10 ml.). This was stirred at 0° for 1 hr., then urea (1 g.) was added, and the solution diluted to 250 ml. and warmed to 80° for 1 hr. A pale fawn solid separated which was filtered off and dissolved in chloroform. The filtrate was extracted with chloroform and the combined chloroform solutions were washed with 10% aqueous sodium hydroxide and dried (Na_2SO_4). Removal

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[6] de Tar, *Organic Reactions*, 1957, **9**, 409.

of the solvent left a pale brown solid which was recrystallised from benzene to give 10-*phenylphenanthridone* (1·625 g.), needles, m. p. 225° (Found: C, 83·8; H, 5·0. $C_{19}H_{13}ON$ requires C, 84·1; H, 4·8%). The mother-liquor (50 ml.) was poured on an alumina column (100 g.). Elution with benzene (1 l.) and benzene–ether (3 : 1; 300 ml.) gave more 10-phenylphenanthridone (0·44 g.). Ether (500 ml.) gave a second product, prisms (0·14 g.), m. p. 197—199° (Found: C, 78·8; H, 5·5; N, 4·75%). Elution with methanol gave a red-brown tar (0·12 g.). The alkali washings were acidified and extracted with chloroform. Concentration of the dried (Na_2SO_4) extract left a brown resin which crystallised from ethanol to give *N*-*o*-hydroxybenzoyldiphenylamine (0·87 g.), prisms, m. p. 192° (Cohn[7] recorded m. p. 193°).

Catalytic Decomposition of the Diazonium Chloride from N-o-*Aminobenzoyldiphenylamine*.—The amine (2·0 g.) was diazotised as described in the previous experiment, and the solution diluted to 200 ml. Copper powder (3 g.) was added, which caused vigorous evolution of nitrogen. After 1 hr. the solution no longer gave a positive test with alkaline β-naphthol. The mixture was filtered and both filtrate and residue extracted with chloroform, whose removal from the dried (Na_2SO_4) extract left a yellow gum which solidified on standing. Recrystallisation from benzene gave 10-phenylphenanthridone (0·63 g.), needles, m. p. 225°. The mother-liquor was poured on alumina (90 g.). Elution with benzene–light petroleum (1 : 1) (300 ml.) and benzene (500 ml.) gave diphenyl-2-carboxyanilide (0·85 g.), needles, m. p. 109—110°, from light petroleum, identical with an authentic specimen. After being heated at 150° for 2 hr. with 100% phosphoric acid, diphenyl-2-carboxyanilide gave fluorenone, m. p. and mixed m. p. 83°. Further elution with benzene (400 ml.) and benzene–ether (2 : 1) (200 ml.) gave more 10-phenylphenanthridone (0·13 g.), needles, m. p. 225°, from light petroleum. Elution with ether and methanol gave a yellow gum (0·16 g.) which could not be crystallised.

Catalytic Decomposition of the Diazonium Fluoroborate from N-o-*Aminobenzoyldiphenylamine*.—The amine (2·0 g.) was diazotised as above and an aqueous solution of sodium fluoroborate (5 g. in 20 ml.) was added slowly to the cold diazonium solution and the mixture stirred for a few minutes. The yellow diazonium fluoroborate was filtered off, washed with cold water (3 × 10 ml.), and dried *in vacuo* overnight. Copper powder (3 g.) was added to the fluoroborate (2·6 g.) in acetone (200 ml.), and the solution stirred for 48 hr. Nitrogen was evolved slowly. The mixture was filtered into water and both filtrate and residue were extracted with chloroform. After removal of the chloroform from the dried (Na_2SO_4) extract, the residue was recrystallised from benzene to give 10-phenylphenanthridone (0·41 g.), needles, m. p. 225°. The mother-liquor (50 ml.) was adsorbed on an alumina column (80 g.). Elution with benzene–light petroleum (1 : 1) (1 l.) gave diphenyl-2-carboxyanilide (0·35 g.), m. p. 108—109°. Further elution with benzene–light petroleum (2 : 1) (600 ml.) gave 10-phenylphenanthridone (0·22 g.), needles, m. p. 225°, from ethanol. Elution with benzene (1200 ml.) gave colourless plates (0·60 g.), m. p. 204—206°, from ethanol (Found: C, 79·2; H, 4·7; N, 4·6%; *M*, 232), which formed a 2 : 4-dinitrophenylhydrazone, orange needles, m. p. 204—206°, from ethyl acetate (Found: C, 63·5; H, 3·9%). Elution with ether and methanol gave a red tar (0·10 g.) which could not be crystallised.

9-*Phenoxyphenanthridine* (*cf. ref.* 1).—9-Chlorophenanthridine[8] (1 g.) was heated with phenol (10 g.) at 150° for 1 hr. Addition of excess of sodium hydroxide solution gave a yellow precipitate which crystallised from ethanol to give 9-*phenoxyphenanthridine* (1·15 g.), needles, m. p. 117—118° (Found: C, 84·1; H, 4·7. $C_{19}H_{13}ON$ requires C, 84·1; H, 4·8%). Walls[1] who incorrectly described this compound as 10-phenylphenanthridone, recorded m. p. 118—119°.

10-*Phenylphenanthridone*.—9-Phenoxyphenanthridine (0·5 g.) was heated at 350° for 2 hr. Recrystallisation of the resultant dark brown solid from ethanol (charcoal) gave 10-phenylphenanthridone (0·3 g.), needles, m. p. 225°, identical with the product obtained as above.

N-o-*Aminobenzoyldi*-p-*tolylamine*.—As described for *N*-*o*-nitrobenzoyldiphenylamine, di-*p*-tolylamine (5 g.) and *o*-nitrobenzoyl chloride (6 g.) in presence of pyridine (10 ml.) and ether (50 ml.) gave N-o-*nitrobenzoyldi*-p-*tolylamine* (7·9 g.), pale yellow plates, m. p. 142—144°, from benzene (Found: C, 73·2; H, 4·9. $C_{21}H_{18}O_3N_2$ requires C, 72·8; H, 5·2%). A solution of this (7·5 g.) in benzene (150 ml.) with Raney nickel (6 g.) was hydrogenated at room temperature and pressure. The catalyst was filtered off and the residue, after removal of the solvent, crystallised from ethanol to give N-o-*aminobenzoyldi*-p-*tolylamine* (6·3 g.), needles, m. p. 166° (Found: C, 79·7; H, 6·3. $C_{21}H_{20}ON_2$ requires C, 79·7; H, 6·3%).

[7] Cohn, *J. prakt. Chem.*, 1900, **61**, 548.

[8] Graebe and Wander, *Annalen*, 1893, **276**, 245.

3-Methyldiphenyl-2'-carboxylic Acid.—Methyl *o*-iodobenzoate (10 g.), *m*-iodotoluene (10 g.), and copper bronze (20 g.) were stirred and heated in a metal-bath at 210°. After 1 hr. the temperature of the bath was gradually raised to 260° and kept thereat until the mixture stopped boiling and maintained at the same temperature for a further hour. The mixture was cooled and extracted with hot ethanol. This extract (150 ml.) was refluxed for 2 hr. with potassium hydroxide (20 g.) in water (20 ml.). Most of the solvent was distilled off, and the residue diluted with water, washed with ether, and acidified with hydrochloric acid. The precipitate was extracted with cold benzene (3 × 20 ml.) and left a residue of diphenic acid. Removal of the benzene left a yellow gum, which crystallised from light petroleum to give *3-methyldiphenyl-2'-carboxylic acid* (1·1 g.), needles, m. p. 100—101° (Found: C, 79·4; H, 5·6. $C_{14}H_{12}O_2$ requires C, 79·25; H, 5·6%).

*3-Methyldiphenyl-2'-carboxy-*p*-toluidide.*—A solution of the acid (0·2 g.) in thionyl chloride (5 ml.) was refluxed for 30 min. Excess of thionyl chloride was removed and the residue dissolved in dry benzene (10 ml.). *p*-Toluidine (0·3 g.) was added, and the mixture warmed on a water-bath for 15 min., then diluted with ether, washed with dilute aqueous acid, and alkali, and dried (Na_2SO_4). The residue, after removal of the solvent, crystallised from light petroleum to give *3-methyldiphenyl-2'-carboxy-*p*-toluidide* (0·2 g.), needles, m. p. 105° (Found: C, 83·8; H, 6·2. $C_{21}H_{19}ON$ requires C, 83·7; H, 6·3%).

4-Methyldiphenyl-2'-carboxylic Acid.—Methyl *o*-iodobenzoate (10 g.), *p*-iodotoluene (10 g.), and copper bronze (20 g.) were treated as for the 3-isomer. After separation from diphenic acid by extraction with cold benzene, the solvent was removed and the brown residue recrystallised from benzene to give *4-methyldiphenyl-2'-carboxylic acid* (1·5 g.), prisms, m. p. 147—149° (Found: C, 79·4; H, 5·8. $C_{14}H_{12}O_2$ requires C, 79·25; H, 5·6%).

*4-Methyldiphenyl-2'-carboxy-*p*-toluidide.*—4-Methyldiphenyl-2'-carboxylic acid, heated with thionyl chloride, as for the 3-isomer, gave 2-methylfluorenone, yellow needles, m. p. 91—92° from light petroleum (b. p. 40—60°). Kruber[9] recorded m. p. 92°. Therefore, the acid (0·2 g.) and *p*-toluidine (0·5 g.) were heated at 200° for 2 hr. The product was dissolved in ether, washed with dilute aqueous acid, and alkali, and dried (Na_2SO_4). After removal of the solvent the residue gave *4-methyldiphenyl-2'-carboxy-*p*-toluidide* (0·08 g.), needles, m. p. 134—135°, from light petroleum (Found: C, 83·7; H, 6·4. $C_{21}H_{19}ON$ requires C, 83·7; H, 6·3%).

Catalytic Decomposition of the Diazonium Chloride from N-o-*Aminobenzoyldi-*p*-tolylamine.*—The amine (3·5 g.), suspended in hydrochloric acid (15 ml.) and water (40 ml.), was diazotised at 0° with sodium nitrite (1 g.) in water (10 ml.). This was stirred at 0° for 1 hr., then urea (1 g.) was added, and the solution diluted to 250 ml. Addition of copper powder (5 g.) caused vigorous evolution of nitrogen and a cream solid separated. After 2 hr. the mixture was filtered and filtrate and residue were extracted with chloroform. The extract was washed with sodium hydroxide solution and dried (Na_2SO_4). Removal of the chloroform left a yellow gum which was dissolved in benzene (50 ml.) and adsorbed on alumina (100 g.). Elution with benzene–light petroleum (1 : 1) (200 ml.) gave 4-methyldiphenyl-2'-carboxy-*p*-toluidide (0·6 g.), needles, m. p. 134—135°, from light petroleum, identical with the authentic specimen. Further elution with benzene–light petroleum (1 : 1) (200 ml.) and benzene (600 ml.) gave a mixture. Benzene–ether and ether gave a brown tar (0·08 g.) and methanol gave a small amount of yellow gum. The mixture was dissolved in benzene and adsorbed on silica gel (70 g.). Elution with benzene–light petroleum (1 : 2) (600 ml.) and (1 : 1) (300 ml.) gave 4-methyldiphenyl-2'-carboxy-*p*-toluidide (1·35 g.). Benzene (800 ml.) gave *3-methyl-10-*p*-tolylphenanthridone* (0·93 g.), needles, m. p. 175—176°, from light petroleum (Found: C, 84·1; H, 5·7. $C_{21}H_{17}ON$ requires C, 84·3; H, 5·7%). Ether gave a little yellow gum.

Catalytic Decomposition of the Diazonium Fluoroborate from N-o-*Aminobenzoyldi-*p*-tolylamine.*—The amine (3·7 g.) was diazotised as above, and aqueous sodium fluoroborate (6 g. in 20 ml.) added to the cold diazonium solution. The yellow diazonium fluoroborate was filtered off and washed with cold water. It began to darken on standing and so it was immediately dissolved in acetone (200 ml.), and copper powder (5 g.) added. A vigorous evolution of nitrogen occurred. After 2 hr. the mixture was filtered into water and both filtrate and residue were extracted with chloroform, whose removal from the dried (Na_2SO_4) extract left an orange gum, which was dissolved in benzene (50 ml.) and adsorbed on silica gel (70 g.). Elution with benzene–light petroleum (1 : 2) (400 ml.) and (2 : 1) (1200 ml.) gave a white solid (2·7 g.), which melted over a wide range. Benzene (200 ml.) gave a yellow gum (0·25 g.) which could not be

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[9] Kruber, *Ber.*, 1932, **65**, 1394.

crystallised. Further elution with benzene (300 ml.) and benzene–ether (1 : 1) (400 ml.) gave prisms (0·43 g.), m. p. 196°, from benzene (Found: C, 82·9; H, 6·2; N, 5·05%; *M*, 225), which was not a ketone. Elution with ether and methanol gave a small amount of brown tar. The mixture obtained by elution with benzene–light petroleum was heated with 100% phosphoric acid (30 g.) at 150° for 2 hr. Water was added and the mixture extracted with chloroform whose removal from the dried (Na_2SO_4) extract left a dark brown glass, which was dissolved in benzene (20 ml.) and adsorbed on alumina (80 g.). Elution with benzene–light petroleum (1 : 10) (700 ml.) gave 2-methylfluorenone (0·82 g.), yellow needles, m. p. 91—92°, from light petroleum (b. p. 40—60°). Benzene–light petroleum (1 : 1) (300 ml.) and benzene (1 l.) gave 3-methyl-10-*p*-tolylphenanthridone (1·1 g.), needles, m. p. 174—175°, from light petroleum. Ether gave a little brown tar.

Thermal Decomposition in Aqueous Solution of the Diazonium Chloride from N-o-*Aminobenzoyldi*-p-*tolylamine*.—The amine (3 g.) was diazotised as above and the diazonium solution diluted to 250 ml. and warmed at 80° for 1 hr. A brown oil separated. The mixture was extracted with chloroform and this extract dried (Na_2SO_4) and concentrated. The residual pale brown gum was dissolved in benzene and adsorbed on alumina (100 g.). Elution with benzene–light petroleum, benzene, and benzene–ether, all gave a white solid melting over a wide range. Methanol gave a brown tar (0·75 g.) which could not be crystallised. The solid was heated with 100% phosphoric acid (15 g.) at 150° for 2 hr. Water was added, and the mixture extracted with chloroform whose removal from the dried (Na_2SO_4) extract left a brown resin, which was dissolved in benzene and adsorbed on alumina (80 g.). Elution with benzene–light petroleum (1 : 3) (200 ml.) gave a little orange solid, m. p. >300°. Benzene (500 ml.) gave 3-methyl-10-*p*-tolylphenanthridone (0·48 g.), needles, m. p. 174—175°, from light petroleum. Benzene–ether (3 : 1) (600 ml.) gave a brown gum (0·925 g.), which yielded more 3-methyl-10-*p*-tolylphenanthridone (0·14 g.) on extraction with light petroleum.

4-*Methyldiphenylamine* (*cf. ref.* 2).—Benz-*p*-toluidide (42·4 g.) and phosphorus pentachloride (43 g.) were heated on a water-bath until no more hydrogen chloride was evolved. The phosphorus oxychloride was distilled off under reduced pressure and the yellow residue was dissolved in ether. Sodium (5·05 g.) in ethanol (200 ml.) was cooled in ice, and phenol (22·5 g.) added. Immediately it had dissolved the ethereal solution of the benzimidoyl chloride was added and the mixture kept overnight. The residue, after removal of the solvent, was washed with water to remove sodium chloride, and recrystallised from ethanol to give *phenyl* N-p-*tolylbenzimidate* (50 g.), needles, m. p. 117—119° (Found: C, 83·7; H, 6·1. $C_{20}H_{17}ON$ requires C, 83·6; H, 5·9%). This (30 g.) was heated at 290° for 2 hr. On cooling, a dark brown glass was obtained which could not be crystallised. The crude *N*-benzoyl-4-methyldiphenylamine was therefore dissolved in ethanol (100 ml.) and refluxed for 2 hr. with potassium hydroxide (30 g.) in water (30 ml.). The ethanol was distilled off, and the residue diluted with water and extracted with chloroform whose removal from the dried (Na_2SO_4) extract left a brown solid which crystallised from aqueous ethanol (charcoal) to give 4-methyldiphenylamine (16 g.), colourless needles, m. p. 88° (Ullmann [10] recorded m. p. 89°).

N-o-*Aminobenzoyl-4-methyldiphenylamine*.—As described for *N*-*o*-nitrobenzoyldiphenylamine, 4-methyldiphenylamine (8 g.) and *o*-nitrobenzoyl chloride (9 g.) in presence of pyridine (10 ml.) and ether (50 ml.) gave 4-*methyl*-N-o-*nitrobenzoyldiphenylamine* (12 g.), pale yellow needles, m. p. 140°, from ethanol (Found: C, 71·9; H, 5·0. $C_{20}H_{16}O_3N_2$ requires C, 72·3; H, 4·8%). This (8 g.) in benzene (150 ml.) with Raney nickel (8 g.) was shaken with hydrogen at atmospheric pressure until the required volume had been absorbed. The Raney nickel was filtered off, and the solution concentrated. The white residue gave N-o-*aminobenzoyl-4-methyldiphenylamine* (7·0 g.), needles, m. p. 134—135°, from ethanol (Found; C, 78·9; H, 6·1. $C_{20}H_{18}ON_2$ requires C, 79·4; H, 6·0%).

9-p-*Tolyloxyphenanthridine*.—9-Chlorophenanthridine (2 g.) was heated with *p*-cresol (10 g.) at 160° for 2 hr. Sodium hydroxide solution was added and the mixture extracted with chloroform whose removal from the dried (Na_2SO_4) extract left a yellow solid which, recrystallised from ethanol, gave 9-p-*tolyloxyphenanthridine* (2·2 g.), needles, m. p. 117° (Found: C, 84·0; H, 5·2. $C_{20}H_{15}ON$ requires C, 84·2; H, 5·3%).

10-p-*Tolylphenanthridone*.—9-*p*-Tolyloxyphenanthridine (1 g.) was heated at 360° for 2 hr. Recrystallisation of the resultant dark brown solid from ethanol (charcoal) gave 10-p-*tolylphenanthridone* (0·7 g.), needles, m. p. 184—186° (Found: C, 84·3; H, 5·5%).

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[10] Ullmann, *Annalen*, 1907, **355**, 325.

Thermal Decomposition in Aqueous Solution of the Diazonium Chloride from N-o-*Aminobenzoyl-4-methyldiphenylamine.*—The amine (2·7 g.), suspended in hydrochloric acid (15 ml.) and water (30 ml.), was diazotised with sodium nitrite (0·7 g.) in water (10 ml.) Urea (0·5 g.) was added and the solution diluted to 200 ml. and warmed to 80° for 1 hr. A brown oil separated. The extract with chloroform was dried (Na_2SO_4) and concentrated. The residual brown gum was washed, with benzene (3 × 15 ml.), leaving a white solid which crystallised from ethanol in plates (0·10 g.), m. p. 218—223° (Found: C, 79·0; H, 5·5%). The benzene solution was adsorbed on alumina (100 g.). Elution with benzene–light petroleum (1 : 1) (300 ml.) gave a small amount of a yellow gum. Benzene–light petroleum (2 : 1) (500 ml.) gave 10-*p*-tolylphenanthridone (0·17 g.), needles, m. p. 184—185°, from light petroleum, identical with the compound obtained as above from 9-*p*-tolyloxyphenanthridine. Further elution with benzene–light petroleum, benzene, and benzene–ether gave a yellow gum which melted over a wide range. Ether and methanol gave a brown tar (0·5 g.). The gum was heated with 100% phosphoric acid (15 g.) at 150° for 2 hr. Water was added, and the mixture extracted with chloroform, whose removal left a dark brown tar which, on extraction with hot benzene, left a black tar which could not be crystallised. The benzene extract was adsorbed on alumina (80 g.). Elution with benzene–light petroleum (1 : 10) (300 ml.) gave a trace of pale green gum. Benzene–light petroleum (1 : 1) (300 ml.) gave 10-*p*-tolylphenanthridone (0·06 g.), needles, m. p. 184—185° from light petroleum. Further elution with benzene–light petroleum and benzene gave a mixture (0·56 g.), which was rechromatographed on silica gel but no pure product was obtained. Elution with ether and methanol gave brown tars.

Catalytic Decomposition of the Diazonium Chloride from N-o-*Aminobenzoyl-4-methyldiphenylamine.*—The amine (2 g.) was diazotised as described above and the diazonium solution diluted to 200 ml. Addition of copper powder (3 g.) caused vigorous evolution of nitrogen and after 1 hr. the solution no longer gave a positive test with alkaline β-naphthol. The mixture was filtered and both filtrate and residue were extracted with chloroform. The extract was dried (Na_2SO_4) and concentrated and the residual dark brown glass was dissolved in benzene and adsorbed on alumina (100 g.). Elution with benzene–light petroleum (2 : 1) (200 ml.) gave 10-*p*-tolylphenanthridone (0·075 g.), m. p. 184—185°. Further elution with benzene–light petroleum, benzene, and benzene–ether gave a mixture. Ether and methanol gave brown tar (0·2 g.). The mixture was heated with 100% phosphoric acid (20 g.) at 150° for 2 hr. Addition of water gave a brown oil which was extracted with chloroform. Removal of the solvent from the dried (Na_2SO_4) extract left a brown oil which was dissolved in benzene and adsorbed on alumina (80 g.). Elution with benzene–light petroleum (1 : 4) (400 ml.) gave a mixture of fluorenones which was purified by vacuum sublimation at 50—70°/10^{-3} mm. Spectroscopy[5] showed this to consist of fluorenone (0·290 g.) and 2-methylfluorenone (0·347 g.). Further elution with benzene–light petroleum (2 : 1) (400 ml.) gave 10-*p*-tolylphenanthridone (0·20 g.), m. p. 183—185°. Benzene and benzene–ether gave a mixture (0·45 g.) and ether gave a brown tar (0·08 g.): the mixture was rechromatographed but no separation was achieved.

N-o-*Aminobenzoyl-4-chlorodiphenylamine.*—As for *N*-*o*-nitrobenzoyldiphenylamine, 4-chlorodiphenylamine (10 g.) and *o*-nitrobenzoyl chloride (12 g.) in presence of pyridine (15 ml.) and ether (50 ml.) gave N-o-*nitrobenzoyl-4-chlorodiphenylamine* (11·2 g.), pale yellow needles, m. p. 112—114°, from ethanol (Found: C, 65·0; H, 4·1. $C_{19}H_{13}O_3N_2Cl$ requires C, 64·7; H, 3·8%). This (8 g.) in benzene (200 ml.) with Raney nickel (8 g.) was hydrogenated at room temperature and pressure. The Raney nickel was filtered off and the solution concentrated. The white residue gave N-o-*aminobenzoyl-4-chlorodiphenylamine* (7·0 g.) in needles, m. p. 163—165°, from ethanol (Found: C, 70·8; H, 4·3. $C_{19}H_{15}ON_2Cl$ requires C, 70·7; H, 4·6%).

9-p-*Chlorophenoxyphenanthridine.*—9-Chlorophenanthridine (2 g.) was heated with *p*-chlorophenol (10 g.) at 150° for 1 hr. Addition of excess of aqueous sodium hydroxide gave a white precipitate which, recrystallised from ethanol, gave 9-p-*chlorophenoxyphenanthridine* (2·6 g.), needles, m. p. 151—152° (Found: C, 74·5; H, 4·2. $C_{19}H_{12}ONCl$ requires C, 74·6; H, 3·9%).

10-p-*Chlorophenylphenanthridone.*—9-p-Chlorophenoxyphenanthridine (1 g.) was heated at 350° for 2 hr. The resulting dark brown solid, on recrystallisation from ethanol (charcoal), gave 10-p-*chlorophenylphenanthridone* (0·75 g.), plates, m. p. 251—252° (Found: C, 74·5; H, 4·2. $C_{19}H_{12}ONCl$ requires C, 74·6; H, 3·9%).

Thermal Decomposition in Aqueous Solution of the Diazonium Sulphate from N-o-*Aminobenzoyl-4-chlorodiphenylamine.*—Sodium nitrite (1 g.) was added slowly with stirring to concentrated sulphuric acid (15 ml.). This solution was cooled to 5° and a cold solution of the amine

(2·5 g.) in acetic acid (15 ml.) was added dropwise, and the mixture stirred at 5° for 2 hr. The mixture was poured on ice (400 g.), and the solution filtered to remove unchanged amine (0·25 g.) and then warmed to 80° for 1 hr. A brown tar separated. This was extracted with chloroform, and the extract dried (Na_2SO_4) and concentrated to give a brown solid, which was dissolved in benzene (30 ml.) and adsorbed on an alumina column (100 g.). Elution with benzene–light petroleum (2 : 1) (300 ml.) gave a little pale green gum. Benzene (600 ml.) gave 10-*p*-chlorophenylphenanthridone (0·51 g.), plates, m. p. 251—252°, from ethanol, identical with the authentic specimen. Further elution with benzene (800 ml.) gave 3-*chloro*-10-*phenylphenanthridone* (0·20 g.), prisms, m. p. 211—212°, from ethanol (Found: C, 74·55; H, 3·9. $C_{19}H_{12}ONCl$ requires C, 74·6; H, 3·9%). Elution with benzene and benzene–ether gave a mixture (0·60 g.). Ether gave a green oil (0·05 g.), and methanol a red-brown tar (0·35 g.). The mixture was heated with phosphoric acid (15 g.) at 150° for 2 hr. Water was added, and a dark brown tar precipitated. This was extracted with chloroform; part was insoluble and was also insoluble in benzene and ethanol, and could not be crystallised. The chloroform solution was dried (Na_2SO_4), and the solvent removed. The residual brown tar was dissolved in benzene and adsorbed on an alumina column (80 g.). Elution with benzene (700 ml.) gave 3-chloro-10-phenylphenanthridone (0·06 g.), m. p. 211—212°. Further elution with benzene and benzene–ether gave a mixture (0·05 g.). Ether and methanol gave a brown tar (0·16 g.).

Catalytic Decomposition of the Diazonium Chloride from N-o-*Aminobenzoyl*-4-*chlorodiphenylamine*.—The amine (4·0 g.), suspended in hydrochloric acid (20 ml.) and water (40 ml.), was diazotised with sodium nitrite (1·2 g.) in water (10 ml.). After being stirred for 1 hr. the mixture was diluted to 250 ml., and unchanged amine (1·6 g.) filtered off. Copper powder (3 g.) was added, and the solution stirred for 2 hr. until it no longer gave a positive test with alkaline β-naphthol. The mixture was filtered and both filtrate and residue were extracted with chloroform. The chloroform was removed from the dried (Na_2SO_4) extract, and the residual yellow gum dissolved in benzene and adsorbed on alumina (100 g.). Elution with benzene (500 ml.) gave 10-*p*-chlorophenylphenanthridone (0·38 g.), plates, m. p. 250—252°, from benzene. Benzene (800 ml.) gave 3-chloro-10-phenylphenanthridone (0·30 g.), prisms, m. p. 211—212°, from ethanol. Further elution with benzene and benzene–ether (1 : 1) gave a mixture (1·23 g.). Ether gave a yellow gum (0·09 g.) and methanol gave a red tar (0·12 g.). The mixture was heated with phosphoric acid (15 g.) at 150° for 2 hr. Water was added, and the mixture extracted with chloroform. The extract was dried (Na_2SO_4) and concentrated, and the residue dissolved in benzene and adsorbed on alumina (80 g.). Elution with benzene–light petroleum (1 : 1) (400 ml.) gave a mixture of fluorenones. This was purified by vacuum sublimation at 50—80°/10^{-3} mm. Spectroscopy[5] showed it to consist of fluorenone (0·273 g.) and 2-chlorofluorenone (0·298 g.). Elution with benzene and benzene–ether gave 3-chloro-10-phenylphenanthridone (0·13 g.), m. p. 211—212°. Ether and methanol gave a little yellow gum.

4-*Methyldiphenyl*-2′-*carboxyanilide*.—4-Methyldiphenyl-2′-carboxylic acid (0·4 g.), prepared as described above, in dry benzene (30 ml.) and thionyl chloride (5 ml.) were refluxed for 30 min. About half the solvent was distilled off, more benzene (50 ml.) was added, and again about half the solvent distilled off. Aniline (1 g.) was added, and the mixture refluxed for 30 min. The solution was washed with dilute aqueous acid, and alkali, and dried (Na_2SO_4). The residue, after removal of the solvent, was recrystallised from aqueous ethanol to give 4-*methyldiphenyl*-2′-*carboxyanilide* (0·42 g.), needles, m. p. 150—152° (Found: C, 83·0; H, 5·8 $C_{20}H_{17}ON$ requires C, 83·6; H, 6·0%). Similarly prepared from 0·4 g. of acid and 1 g. of amine were *diphenyl*-2-*carboxy*-p-*toluidide* (0·5 g.), needles, m. p. 143—145° from aqueous ethanol (Found: C, 83·3; H, 5·7%), *diphenyl*-2-*carboxy*-p-*chloroanilide* (0·45 g.), plates, m. p. 165—167°, from ethanol (Found: C, 73·9; H, 4·6. $C_{19}H_{14}ONCl$ requires C, 74·15; H, 4·5%), and (from 4-chlorodiphenyl-2′-carboxylic acid[11]) 4-*chlorodiphenyl*-2′-*carboxyanilide* (0·45 g.), needles, m. p. 196—198°, from ethanol (Found: C, 74·6; H, 4·4%).

Conversion of Anilides into Fluorenones.—Each of the four anilides (*ca.* 0·3 g.) was heated with 100% phosphoric acid (10 g.) at 150° for 2 hr. The product was diluted with water and extracted with chloroform. The dried (Na_2SO_4) extract was concentrated, and the residue purified by vacuum sublimation at 50—80°/10^{-3} mm. to give the corresponding fluorenones. Thus diphenyl-2-carboxy-*p*-toluidide (0·2965 g.) gave fluorenone (0·180 g.), m. p. and mixed m. p. 83°; 4-methyldiphenyl-2′-carboxyanilide (0·301 g.) gave 2-methylfluorenone (0·193 g.), m. p. 92°; diphenyl-2-carboxy-*p*-chloroanilide (0·300 g.) gave fluorenone (0·171 g.), m. p. and

[11] Heilbron, Hey, and Wilkinson, *J.*, 1938, 113.

mixed m. p. 83°; 4-chlorodiphenyl-2′-carboxyanilide (0·305 g.) gave 2-chlorofluorenone (0·208 g.), m. p. and mixed m. p. 123°.

4-*Methoxycarbonyldiphenylamine.*—Methyl *p*-hydroxybenzoate (45 g.) was added to a cold solution of sodium (6·2 g.) in anhydrous ethanol (250 ml.). When solution was complete, *N*-phenylbenzimidoyl chloride in dry ether (250 ml.) was added. [The benzimidoyl chloride was prepared by heating benzanilide (48 g.) and phosphorus pentachloride (52 g.) at 100° until no more hydrogen chloride was evolved, and then distilling off phosphorus oxychloride under reduced pressure.] The mixture was allowed to stand overnight, then the precipitated sodium chloride was filtered off. The filtrate was evaporated to dryness, and crystallisation of the residue from ethanol gave p-*methoxycarbonylphenyl* N-*phenylbenzimidate* (59 g.), needles, m. p. 108—109° (Found: C, 75·6; H, 5·1. $C_{21}H_{17}O_3N$ requires C, 76·1; H, 5·1%). The benzimidate (50 g.) was heated at 300° for 2 hr. Crystallisation of the product from ethanol (charcoal) gave N-*benzoyl*-p-*methoxycarbonyldiphenylamine* (42 g.), prisms, m. p. 112—114° (Found: C, 76·5; H, 5·0. $C_{21}H_{17}O_3N$ requires C, 76·1; H, 5·1%). The benzoyl derivative (35 g.) in ethanol (100 ml.) was refluxed for 2 hr. with potassium hydroxide (50 g.) in water (50 ml.). Most of the ethanol was distilled off and the free acid was precipitated with hydrochloric acid, filtered off, and washed with hot water (3 × 50 ml.). Recrystallisation from benzene gave *diphenylamine*-4-*carboxylic acid* (16·5 g.), plates, m. p. 156—157° (Found: C, 72·8; H, 5·1. $C_{13}H_{11}O_2N$ requires C, 73·2; H, 5·2%). Dry hydrogen chloride was passed into a solution of the acid (7 g.) in anhydrous methanol (50 ml.) until the solution was saturated. After being boiled under reflux for 2 hr. the solvent was distilled off, and the residue dissolved in ether. The ethereal solution was washed with aqueous sodium carbonate and with water and dried (Na_2SO_4). Removal of the solvent left a brown solid which, on crystallisation from ethanol, gave 4-*methoxycarbonyldiphenylamine* (6·2 g.), needles, m. p. 115—117° (Found: C, 73·8; H, 5·6. $C_{14}H_{13}O_2N$ requires C, 74·0; H, 5·7%). Neither the acid nor its methyl ester could be converted into the *o*-nitrobenzoyl derivative by reaction with *o*-nitrobenzoyl chloride.

Grateful acknowledgment is made to the Department of Scientific and Industrial Research for a Maintenance Award to T. M. M.

King's College (University of London),
Strand, London, W.C.2.

[*Received, November 26th,* 1958.]