# 13. *Symmetrical Triad Prototropic Systems. Part IX. The Influence of Polynuclear Aryl Groups upon Mobility and Equilibrium in the αγ-Diarylmethyleneazomethine System.*

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OWING to the capacity of aryl groups to confer on an attached carbon atom increased toleration for an ionic charge of either sign (± *T* effect), such groups are capable of activating both prototropic systems (I) (Shoppee, J., 1928, 2567; Ingold and Shoppee, J., 1929, 447) and anionotropic systems (II) (Burton and Ingold, J., 1928, 904; *Proc. Leeds Phil. Soc.*, 1929, **1**, 421; Burton, J., 1928, 1650). The stabilisation of the electron septet in the formation of free radicals is referred to the same cause, and the further deduction is made (Burton and Ingold) that polynuclear aryl groups should act more powerfully than phenyl in promoting dissociation into free radicals in the order: 9-phenanthryl > α-anthryl > α-naphthyl > β-naphthyl > *p*-diphenylyl > *m*-diphenylyl > phenyl. This serial order has been

(I.)

$\mathrm{Ar{-}\overset{\ominus}{C}H\cdot CH{:}CHAr'}$

$\mathrm{Ar{-}\overset{\oplus}{C}H\cdot CH{:}CHAr'}$

(II.)

confirmed in the four cases for which evidence is available, namely: α-naphthyl > β-naphthyl > *p*-diphenylyl > phenyl. Since the foregoing theoretical sequence is to be interpreted as representing capacity for duplex polar adjustment ($\pm T$), it might also prove to correspond to the order in which the groups concerned exhibit the effects designated $+T$ and $-T$ separately. This possibility, although not logically compulsory, is attractively simple and if true would mean that the order illustrated is that in which the groups facilitate first aromatic side-chain reactions requiring electron accession (Type A) and secondly those dependent on electron recession (Type B). Moreover, the same order would hold in relation to the conferment of anionotropic mobility, and yet again for the conferment of prototropic mobility.

As regards side-chain reactivity Ingold and Patel (*J. Indian Chem. Soc.*, 1930, 95) have found that the velocity coefficients for acid hydrolysis of aryl methyl bromides (Type A), and for reduction of these compounds (Type B), conform to a sequence identical with that given above: α-naphthyl > β-naphthyl > *p*-diphenylyl > *m*-diphenylyl > phenyl. Moreover, Burton has shown recently (J., 1931, 760) that for the facilitation of anionotropy in the simple three-carbon system

$$\mathrm{Ar{\cdot}CH(OH){\cdot}CH{:}CH_2 \rightleftharpoons Ar{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OH}$$

the mobility sequence is α-naphthyl > β-naphthyl > phenyl.

The present paper completes the comparison instituted above and describes the effect of some polynuclear aryl groups on mobility (and equilibrium) in the methyleneazomethine prototropic system (III $\rightleftharpoons$ IV).

$$\text{(III.)}\quad \mathrm{Ar{\cdot}CH{:}N{\cdot}CH_2Ph} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{Ar{\cdot}CH_2{\cdot}N{:}CHPh}\quad \text{(IV.)}$$

(Ar = 9-phenanthryl, α-naphthyl, β-naphthyl, *p*-diphenylyl, and *m*-diphenylyl.)

*Mobility*.—The effect of the introduction of the variants Ar on the velocity of interconversion of the isomerides (III, IV) under standard conditions of temperature and catalysis is as follows:

| Ar | 9-Phenanthryl. | α-$C_{10}H_7$. | β-$C_{10}H_7$. | *p*-$C_6H_4$Ph. | *m*-$C_6H_4$Ph. |
|---|---|---|---|---|---|
| $k_1 + k_2$, hr.$^{-1}$ | 2·27 | 3·49 | 3·04 | 2·93 | 2·33 |

With the exception of 9-phenanthryl (see below), the mobility sequence, which necessarily omits the phenyl group, is identical with that given by Ingold and Burton.

The low degree of mobility conferred by the 9-phenanthryl group is unexpected; although, owing to the largely one-sided nature of the equilibrium attained, only the velocity constants given by isomeride (III) could accurately be determined, there is no doubt that the true value is considerably less instead of being greater than that of the α-naphthyl group. This result indicates the operation of some de-activating influence, whose character may be polar or steric or both. Nothing is known with regard to the effect on mobility of steric influence (the term is used with full recognition of the fact that its origin must fundamentally be polar), but it may be presumed to cause considerable disturbance in cases of *o*-substitution (cf. phenanthryl, α-naphthyl), and further work on this field is projected. The expectation of polar disturbances arises from the circumstance that the tentative application of a $\pm T$-relation to reactions involving only electron accession or only electron recession is most likely to be true in the absence of an inductive effect and certain to be untrue as a generality in its presence. But the case of toluene shows that the lateral linking of an aromatic compound with a side chain must in general be the seat of a dipole moment, and must therefore constitute part of the path of an inductive effect. The degree of consistency demonstrated in this work and that already referred to can probably be interpreted as indicating that the inductive effect referred to is small in most cases; but there is no independent indication that this holds for phenanthrene derivatives, and it may be significant that the phenanthrene skeleton is the only structure here studied which is devoid of an axis of symmetry perpendicular to the lateral linking.

*Equilibrium*.—The equilibria attained by the system (III $\rightleftharpoons$ IV), under the influence of either 0·145*N*- or 1·45*N*-alcoholic sodium ethoxide at 82° or 85° respectively, by introduction of the variants Ar are as follows:

| Ar | 9-Phenanthryl. | $\alpha$-$C_{10}H_7$. | $\beta$-$C_{10}H_7$. | $p$-$C_6H_4Ph$. | $m$-$C_6H_4Ph$. |
|---|---|---|---|---|---|
| *K* | 4·41 | 2·70 | 0·695 | 0·639 | 0·785 |
| Isomeride (III), % | 18·5 | 27·0 | 59·0 | 61·0 | 56·0 |

In preceding investigations on the effect of substitution on equilibrium, such substituents (*m* or *p*) were introduced at a relatively large distance from the seat of reaction; the various cases studied were therefore largely independent of steric influences, and suitable for direct comparison. Since we are now dealing with bulky groups, equivalent in two cases to the presence of an *o*-substituent, the numerical values tabulated above must reflect, to some degree at present unknown, the operation of steric influences. Nevertheless, the results place the groups, with the exception of *m*-diphenylyl, in the order theoretically deduced for radical stability.

A new synthesis of phenanthrene-9-carboxylic acid, which is convenient for the production of small quantities (25—50 g.), and the preparation of phenanthrene-9-aldehyde are described.

Stephen's method for the preparation of aldehydes (J., 1925, **127**, 1874) fails with 4-cyanodiphenyl, more than 90% of which can be recovered. The alternative method of Sonn and Müller (*Ber.*, 1919, **52**, 1927), which involves reduction of the imino-chloride obtained by the action of phosphorus pentachloride on the anilide of diphenyl-4-carboxylic acid, affords some diphenyl-4-aldehyde, but the bulk of the material is unaffected. Both methods succeed with the more soluble compounds of the *m*-series; 3-cyanodiphenyl and the *anilide* of diphenyl-3-carboxylic acid each yield 40—50% of *diphenyl-3-aldehyde*, which furnishes the usual crystalline derivatives.

Attempts to prepare diphenyl-3-sulphonic acid, from which the difficultly obtainable 3-cyanodiphenyl might be producible, failed; sulphonation of 4-aminodiphenyl under various conditions gave, not the 3-sulphonic acid, but 4-aminodiphenyl-4′-sulphonic acid (Carnelley and Schleselman, J., 1886, **49**, 380); the latter on deamination has now been shown to give diphenyl-4-sulphonic acid, which establishes its constitution.

## EXPERIMENTAL.

The azomethines were prepared by methods already described (J., 1931, 1225; 1932, 703): if solid, they were recrystallised to const. m. p.; if liquid, repeatedly fractionated in a high vac. The azomethines described below are stable substances; β-naphthylidene- and 4-phenylbenzylidene-benzylamine, however, are photo-sensitive.

*Interconversion of Tautomerides.*—The standard conditions were: catalyst, 0·145*N*-alc. NaOEt; temp., 82°. The product was isolated as described (*loc. cit.*), and the progress of interconversion followed by thermal analysis of mixtures of *p*-nitrophenylhydrazones. The hydrazones obtained by fission of the isomerides (III) were used without further purification for the construction of temp.-composition diagrams. All such diagrams were of the two-branch type, and the products of the interconversion expts. strictly binary in character; all m. p.'s were determined under identical conditions in the same apparatus.

The following table gives the m. p.'s, yields obtained by fission of the azomethines with *p*-nitrophenylhydrazine acetate, and analytical data for the following aldehyde-*p*-nitrophenylhydrazones:

|  | M. p. (purif.). | M. p. (crude). | Yield, %. | Found. |  | Calc. |  |
|---|---|---|---|---|---|---|---|
|  |  |  |  | C, %. | H, %. | C, %. | H, %. |
| *Phenanthrene*-9- | 265° | 265° | 101 | 73·9 | 4·45 | 73·9 | 4·4 |
| α-Naphthyl- | 234·5 | 234 | 101 | — | — | — | — |
| *β-Naphthyl-* | 230 | 230 | 103 | 69·9 | 4·5 | 70·1 | 4·5 |
| *Diphenyl*-4- | 216·5 | 216 | 102 | 72·0 | 4·8 | 71·9 | 4·8 |
| *Diphenyl*-3- | 188 | 187·5 | 101·5 | 71·6 | 4·6 | 71·9 | 4·8 |

### 9-*Phenanthryl Compounds.*

*Phenanthrene*-9-*carboxylic Acid.*—9-Bromophenanthrene (b. p. 225°/15 mm., m. p. 63°; Austin, J., 1908, **93**, 1763) (77 g.) was dissolved in dry $Et_2O$ (370 g.) and anisole (150 g.) and treated with Mg (7·2 g.), and the solution of 9-phenanthrylmagnesium bromide filtered into a flask containing dry $CO_2$ and stirred mechanically. After 4—5 hr., the $CO_2$ latterly being bubbled through the liquid, ice-water was added, followed by 2*N*-$H_2SO_4$, the mixture stirred for 1 hr., and the emulsion filtered. The ppt. was washed with a little $Et_2O$, dissolved in $NH_3$ aq.

and filtered into an excess of HCl aq. The phenanthrene-9-carboxylic acid obtained (25 g.) had m. p. 250—251° after one crystn. from EtOH (Found : C, 81·1; H, 4·6. Calc. : C, 81·1; H, 4·55%); 8 g. of crude acid were extracted from the ether–anisole liquor by NaOH aq.

9-*Phenanthroyl chloride*, prepared from the acid and $SOCl_2$ on the steam-bath, had b. p. 240°/13 mm. and separated from $C_6H_6$ in pale yellow needles, m. p. 102° (Found : C, 75·3; H, 3·9. $C_{15}H_9OCl$ requires C, 74·9; H, 3·8%). It was converted by boiling EtOH into the ethyl ester, m. p. 61°; by MeOH into *methyl phenanthrene*-9-*carboxylate*, long needles, m. p. 115°, from MeOH (Found : C, 81·2; H, 5·1. $C_{16}H_{12}O_2$ requires C, 81·4; H, 5·1%); by $NH_3$ in dry $Et_2O$ into the amide, m. p. 226°; and by aniline (2 mols.) in warm $CHCl_3$ into the *anilide*, m. p. 218° after crystn. from much EtOH or from acetone–ligroin (b. p. 60—80°) (Found : C, 84·9; H, 5·1. $C_{21}H_{15}ON$ requires C, 84·85; H, 5·1%).

*Phenanthrene*-9-*aldehyde*.—The anilide (10 g.) was treated with $PCl_5$ (7 g.) in $C_2H_2Cl_4$ at 140—150°, the $POCl_3$ removed under reduced press., and the iminochloride dissolved in $C_2H_2Cl_4$ and slowly added to $SnCl_2$ (28 g.) in ethereal HCl (250 c.c.) at 0°. After some hr. the orange aldimine stannichloride was washed with $Et_2O$ and hydrolysed with hot 2*N*-HCl. *Phenanthrene*-9-*aldehyde* (6 g.) separated from ligroin (b. p. 60—80°) in rosettes of pale yellow prisms, m. p. 101° (Found : C, 87·6; H, 4·85. $C_{15}H_{10}O$ requires C, 87·4; H, 4·9%). The *semicarbazone* had m. p. 222—222·5° after crystn. from MeOH or EtOH (Found : C, 72·5; H, 5·0. $C_{16}H_{13}ON_3$ requires C, 73·0; H, 5·0%). The aldehyde is converted by MeOH and a trace of HCl into an oily acetal (or semiacetal), which readily regenerates the aldehyde when boiled with an excess of 2*N*-HCl.

Oxidation of the aldehyde with 3% $KMnO_4$ aq. and $Na_2CO_3$ aq. gave phenanthrene-9-carboxylic acid, m. p. 250° after two crystns. from EtOH.

9-*Phenanthrylidenebenzylamine* (as III) separated from $Et_2O$–ligroin (b. p. 40—60°) in almost colourless, well-formed prisms, m. p. 72—72·5° (Found : C, 89·3; H, 5·8. $C_{22}H_{17}N$ requires C, 89·5; H, 5·8%). The phenanthrene-9-aldehyde used was obtained from the pure semicarbazone and 2*N*-$H_2SO_4$.

*Phenanthrene*-9-*aldoxime*, prepared in good yield by Bamberger and Scheutz's method (*Ber.*, 1901, **34**, 2024), separated from dil. EtOH in colourless iridescent plates, m. p. 155° (Found : C, 81·5; H, 5·2. $C_{15}H_{11}ON$ requires C, 81·4; H, 5·0). With ethereal HCl, it gave a yellow hydrochloride, m. p. 126—127°. Dehydration of the oxime with boiling $Ac_2O$ produced 9-cyanophenanthrene, needles from EtOH; m. p. 109° (Werner and Künz, *Annalen*, 1902, **321**, 327, give m. p. 103°) (Found : C, 88·3; H, 4·5; N, 6·9. Calc. : C, 88·6; H, 4·5; N, 6·9%) : this was hydrolysed by 50% $H_2SO_4$ and AcOH to phenanthrene-9-carboxylic acid, m. p. 250°.

9-*Phenanthrylmethylamine*.—Reduction of the oxime with 3% Na–Hg and AcOH yielded the *base* as a colourless solid, m. p. 107° after crystn. from $Et_2O$–ligroin (b. p. 40—60°) (Found : C, 86·8; H, 6·5. $C_{15}H_{13}N$ requires C, 87·0; H, 6·3%) : *picrate*, needles from EtOH containing a little acetone, m. p. 241° (decomp.) (Found : C, 57·7; H, 3·7. $C_{21}H_{16}O_7N_4$ requires C, 57·8; H, 3·7%); *benzoate*, needles from $CHCl_3$–ligroin (b. p. 60—80°), m. p. 167° (Found : C, 80·3; H, 5·8. $C_{22}H_{19}O_2N$ requires C, 80·2; H, 5·8%); *acetyl* derivative, m. p. 182·5° after crystn. from $Ac_2O$ and from EtOH (Found : C, 81·7; H, 6·4. $C_{17}H_{15}ON$ requires C, 81·9; H, 6·1%).

*Benzylidene*-9-*phenanthrylmethylamine* (as IV).—The *azomethine* separated from $C_6H_6$–ligroin in radiating aggregates of colourless needles, m. p. 103·5° (Found : C, 89·7; H, 5·8. $C_{22}H_{17}N$ requires C, 89·5; H, 5·8%).

Mixtures of phenanthrene-9-aldehyde- and benzaldehyde-*p*-nitrophenylhydrazones melted as follows (A denotes the latter) :

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| A, % | 0 | 20·0 | 42·1 | 62·1 | 79·0 | 90·0 | 100 |
| M. p. | 265° | 250° | 234° | 213·5° | 190° | 186° | 190° |

*Interconversion.* (*a*) With *N*-NaOEt at 84° :

Isomeride (III) used.

| Time, hr. | Yield, %. | M. p. | Isomeride (IV), %. |
|---|---|---|---|
| 1 | 98 | 185°* | 81·5 |
| 1 | 98 | 185·5 | 81·5 |

Isomeride (IV) used.

| Time, hr. | Yield, %. | M. p. | Isomeride (IV), %. |
|---|---|---|---|
| 1 | 100 | 185°† | 81·5 |

* To 10·1 mg. of this equilibrium specimen, 1·0 mg. of phenanthrene-9-aldehyde-*p*-nitrophenylhydrazone was added; the mixture had m. p. 200° (calc., 199°).

† 10·3 Mg. of this equilibrium specimen and 1·4 mg. of phenanthrene-9-aldehyde-*p*-nitrophenylhydrazone gave a mixture, m. p. 201·5° (calc., 202°).

Equilibrium : IV (81·5%) $\rightleftarrows$ III (18·5%)

The proximity of the eutectic (at 82·5% of isomeride IV) to the equilibrium point affects adversely the sharpness of the m. p.'s.

(*b*) With 0·145*N*-NaOEt at 82°:

Isomeride (III) used.

| Time, min. | Yield, %. | M. p. | Isomeride (IV), %. | $k_1 + k_2$, hr.$^{-1}$. |
|---|---|---|---|---|
| 0 | 101, 102 | 265° | 0 | — |
| 5 | 101 | 254—254·5 | 14 | 2·26 |
| 10 | 98 | 245 | 26 | 2·30 |
| 15 | 101 | 237·5 | 36 | 2·33 |
| 20 | 102 | 233·5 | 41 | 2·10 |
| 25 | 98 | 224·5 | 50 | 2·28 |
| 30 | 98 | 221 | 54 | 2·18 |
| 35 | 99 | 214—214·5 | 61 | 2·36 |
| 40 | 99 | 210 | 65 | 2·39 |
| 120 | 98 | 185 | 81·5 | — |

Isomeride (IV) used.

| Time, min. | Yield, %. | M. p. | Isomeride (IV), %. | $k_1 + k_2$, hr.$^{-1}$. |
|---|---|---|---|---|
| 120 | 100 | 185° | 81·5 | — |
| 40 | 101 | 182—183·5* | 83 | — |
| 15 | 100 | 184 | 85 | — |
| 10 | 100 | 185·5 | 85·5 | — |
| 5 | 99 | 187 | 92·5 | — |
| 0 | 100 | 190 | 100 | — |

* This is very close to the eutectic.

Equilibrium: IV (81·5%) $\rightleftharpoons$ III (18·5%); $k_1 + k_2$ (mean of values derived from isomeride III) = 2·27 hr.$^{-1}$; $k_1/k_2 = 4{\cdot}41$; $k_1 = 1{\cdot}85$; $k_2 = 0{\cdot}42$.

Owing to the one-sided nature of the equilibrium and to the form of the temp.–composition diagram, reliable vel. consts. are obtained only from isomeride (III).

### β-*Naphthyl Compounds.*

β-Naphthanilide was converted by $PCl_5$ into the imino-chloride, which was reduced with $SnCl_2$ in ethereal HCl to yield β-naphthaldehyde, m. p. 59°.

β-*Naphthylidenebenzylamine* (as III) separated from EtOH in colourless plates, m. p. 83·5° (Found: C, 88·0; H, 6·05. $C_{18}H_{15}N$ requires C, 88·1; H, 6·2%).

β-*Naphthylmethylamine.*—ω-Bromo-β-methylnaphthalene, m. p. 56°, b. p. 180—182°/20 mm., obtained by bromination of β-methylnaphthalene at 200°, condensed with potassium phthalimide (1 mol.) at 180° to give *phthalo*-β-*naphthylmethylimide*, m. p. 150—151°, needles from acetone–EtOH (Found: C, 79·7; H, 4·6. $C_{19}H_{13}O_2N$ requires C, 79·4; H, 4·6%). Fission of the phthalimide with $N_2H_4$ produced β-naphthylmethylamine, m. p. 59—60°, b. p. 180°/24 mm.: *picrate*, needles from EtOH, m. p. 230—231° (decomp.) (Found: C, 52·5; H, 3·8. $C_{17}H_{14}O_7N_4$ requires C, 52·8; H, 3·5%); *benzoate*, m. p. 163° after crystn. from $CHCl_3$–ligroin (Found: C, 76·8; H, 6·1. $C_{18}H_{17}O_2N$ requires C, 77·4; H, 6·2%).

*Benzylidene*-β-*naphthylmethylamine* (as IV) separated from EtOH in colourless plates, m. p. 85·5° (Found: C, 88·0; H, 6·4%).

Mixtures of β-naphthaldehyde-*p*-nitrophenylhydrazone and benzaldehyde-*p*-nitrophenylhydrazone melted as follows (A denotes the latter):

| A, % | 0 | 17·9 | 24·3 | 31·1 | 33·4 | 43·0 | 54·0 | 58·5 | 63·0 | 80·5 | 100 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| M. p. | 230° | 222° | 219° | 215° | 213·5° | 205° | 193° | 188° | 182° | 177·5° | 190° |

*Interconversion.* (*a*) With 1·45*N*-NaOEt at 85°:

| Isomeride used. | Time at 85° with NaOEt, hr. | Yield, %. | M. p. | Isomeride (IV), %. |
|---|---|---|---|---|
| III | 1 | 97·5 | 206·5° | 41 |
| IV | 1 | 97 | 207 | 41 |

Equilibrium: IV (41·0%) $\rightleftharpoons$ III (59·0%).

(*b*) With 0·145*N*-NaOEt at 82°:

Isomeride (III) used.

| Time at 82° with NaOEt, min. | Yield, %. | M. p. | Isomeride (IV), %. | $k_1 + k_2$, hr.$^{-1}$. |
|---|---|---|---|---|
| 0 | 103 | 230° | 0 | — |
| 5 | 100·5 | 227 | 7·5 | (2·42) |
| 7·5 | 100 | 225 | 12 | 2·76 |
| 10 | 100 | 223 | 16 | 2·96 |
| 12·5 | 98 | 221·5 | 18·5 | 2·88 |
| 15 | 101 | 220 | 22 | 3·08 |
| 20 | 101 | 218 | 26 | 3·01 |
| 30 | 100 | 214 | 32·3 | 3·09 |
| 60 | 98 | 208·5 | 39 | 3·01 |
| 90 | 97 | 207 | 41 | — |

Isomeride (IV) used.

| Time at 82° with NaOEt, min. | Yield, %. | M. p. | Isomeride (IV), %. | $k_1 + k_2$, hr.$^{-1}$. |
|---|---|---|---|---|
| 90 | 98 | 207° | 41 | — |
| 60 | 99 | 205 | 43 | 3·48 |
| 30 | 101 | 198 | 50 | (3·76) |
| 20 | 100 | 185 | 61 | 3·24 |
| 17·5 | 93·5 | 181 | 64 | 3·22 |
| 10 | 101 | 172·5 | 73·5 | 3·22 |
| 7·5 | 101 | 178 | 81·3 | 3·04 |
| 5·5 | 100 | 180·7 | 85·5 | 3·07 |
| 5 | 100 | 181·5 | 86·5 | 3·11 |
| 0 | 100 | 190 | 100 | — |

Equilibrium: IV (41·0%) $\rightleftharpoons$ III (59·0%); $k_1 + k_2$ (mean) = 3·08 hr.$^{-1}$; $k_1/k_2 = 0{\cdot}695$; $k_1 = 1{\cdot}26$; $k_2 = 1{\cdot}82$.

### α-*Naphthyl Compounds.*

α-Naphthaldehyde, prepared in the same way as the β-compound and purified through the bisulphite compound, had b. p. 156°/15 mm., 150°/9 mm.

β-*Naphthylidenebenzylamine* (as III) was obtained as a pale yellow oil, b. p. 208°/0·4 mm. (Found : C, 87·8; H, 6·0. $C_{18}H_{15}N$ requires C, 88·2; H, 6·2%).

*Phthalo*-β-*naphthylmethylimide*, m. p. 175—176° after crystn. from acetone–EtOH (Found : C, 79·0; H, 4·6. $C_{19}H_{13}O_2N$ requires C, 79·4; H, 4·6%), on fission with $N_2H_4$ gave β-naphthylmethylamine, b. p. 174—175°/19 mm.: *picrate*, needles, m. p. 227° (decomp.), from EtOH (Found : C, 52·9; H, 3·7. $C_{17}H_{14}O_7N_4$ requires C, 52·8; H, 3·5%); *benzoate*, rectangular plates, m. p. 142·5—143°, from $CHCl_3$–ligroin (b. p. 60—80°) (Found: C, 77·0; H, 6·15. $C_{18}H_{17}O_2N$ requires C, 77·4; H, 6·15%).

*Benzylidene*-α-*naphthylmethylamine* (as IV) separated from EtOH in pearly plates, m. p. 55·5° (Found : C, 88·2; H, 6·2%).

Mixtures of α-naphthaldehyde- and benzaldehyde-*p*-nitrophenylhydrazone melted as follows (A denotes the latter) :

| A, % | 0 | 20·1 | 33·7 | 43·8 | 56·4 | 69·9 | 72·3 | 76·2 | 85·0 | 100 |
|---|---|---|---|---|---|---|---|---|---|---|
| M. p. | 234° | 224° | 217° | 210° | 200° | 185° | 181° | 178° | 183° | 190° |

*Interconversion.* (*a*) With 1·45*N*-NaOEt at 85° :

| Isomeride used. | Time at 85° with NaOEt, hr. | Yield, %. | M. p. | Isomeride (IV), %. |
|---|---|---|---|---|
| III | 1 | 100 | 178·5° | 73 |
| IV | 1 | 99 | 176 | 74 |

Equilibrium : IV (73·0%) $\rightleftharpoons$ III (27·0%).

The eutectic mixture contains 74% of isomeride (IV), and the coincidence of this with the equilibrium mixture renders difficult the determination of the m. p.'s of equilibrium specimens.

(*b*) With 0·145*N*-NaOEt at 82°. The isomeride (III) yielded somewhat variable constants as compared with (IV); since (III) is a liquid and therefore of uncertain purity, the constants given by (IV) are preferred.

| Isomeride used. | Time at 82° with NaOEt, min. | Yield, %. | M. p. | Isomeride (IV), %. | $k_1 + k_2$, hr.$^{-1}$. Calc. from zero time. | Calc. by time diff. |
|---|---|---|---|---|---|---|
| III | 0 | 101, 102·5 | 234° | 0 | — | — |
| | 2·5 | 101 | 230 | 8 | 2·84 | 2·84 |
| | 5 | 97·5 | 226·5 | 15 | 2·76 | 3·10 |
| | 7·5 | 96 | 225 | 18 | 2·27 | (1·27) |
| | 10 | 96 | 223 | 22 | 2·15 | (1·81) |
| | 12·5 | 98 | 219·2 | 29 | 2·43 | 3·70 |
| | 15 | 100 | 216 | 35 | 2·60 | 3·35 |
| | 35 | 99 | 200 | 56·5 | 2·55 | 2·16 |
| | 90 | 101 | 178·5 | 73 | — | — |
| IV | 90 | 99 | 176 | 74* | — | |
| | 35 | 100 | 178 | 76 | (3·76) | |
| | 15 | 100 | 183 | 84·5 | 3·41 | |
| | 12·5 | 99 | 183·5 | 86 | 3·51 | |
| | 10 | 100 | 184·5 | 88 | 3·52 | |
| | 7·5 | 100 | 185·5 | 90·5 | 3·47 | |
| | 5 | 100 | 187 | 93·5 | 3·31 | |
| | 2·5 | 101, (103) | 188, (188) | 96·3 | 3·43 | |
| | 0 | 100 | 190 | 100 | — | |

* This is also the eutectic mixture.

Equilibrium : IV (73·0%) $\rightleftharpoons$ III (27·0%); $k_1 + k_2$ (mean of values derived from isomeride IV) = 3·44 hr.$^{-1}$; $k_1/k_2 = 2·70$; $k_1 = 2·51$; $k_2 = 0·93$.

### p-*Diphenyl Compounds.*

4-Aminodiphenyl (as hydrochloride) was smoothly converted (contrast Ferriss and Turner, J., 1920, **117**, 1148; Gull and Turner, J., 1929, 498) by the Sandmeyer reaction into 4-cyanodiphenyl (yield, 45%), which was removed by steam at 110—120°, extracted and dried in $Et_2O$, and obtained as a water-clear liquid, b. p. 190—193°/20 mm., m. p. 86°.

*Diphenyl*-4-*carboxyanilide*, prepared from the *acid chloride* (b. p. 185—186°/12 mm., m. p. 107—108° after crystn. from $C_6H_6$–ligroin. Found : C, 72·8; H, 4·4. $C_{13}H_9OCl$ requires

C, 72·0; H, 4·2%) and hot aniline (2 mols.), formed colourless needles, m. p. 220°, from EtOH (Found : C, 84·0; H, 5·5. $C_{19}H_{15}ON$ requires C, 83·5; H, 5·5%).

Diphenyl-4-aldehyde was readily obtained by Hey's modification (J., 1931, 2476) of the Gattermann–Koch synthesis; m. p. 60° after crystn. from ligroin (b. p. 80—100°). The *semicarbazone* separated from EtOH in plates, m. p. 243° (decomp.) (Found : C, 70·3; H, 5·6. $C_{14}H_{13}ON_3$ requires C, 70·3; H, 5·5%).

4-*Phenylbenzylidenebenzylamine* (as III) separated in felted needles from $Et_2O$–ligroin, $CCl_4$–ligroin, or MeOH; it melted at 52°, resolidified at 52—53°, and melted again at 60° (Found : C, 88·8; H, 6·3. $C_{20}H_{17}N$ requires C, 88·6; H, 6·3%).

Diphenyl-4-aldoxime was obtained quantitatively from alc. solutions of the aldehyde and $NH_2{\cdot}OH$ ($Na_2CO_3$); m. p. 150° (cf. Gattermann, *Annalen*, 1906, **347**, 381). Dehydration with hot $Ac_2O$ gave 4-cyanodiphenyl, m. p. 86°.

4-*Phenylbenzylamine* was readily obtained by reduction of the aldoxime with 3% Na–Hg and AcOH as a water-clear liquid, b. p. 195°/20 mm., solidifying to crystals, m. p. 53—54° (Found : C, 84·9; H, 7·2. $C_{13}H_{13}N$ requires C, 85·2; H, 7·2%) : *picrate*, leaflets, m. p. 218° (decomp.), from MeOH (Found : C, 55·3; H, 4·0. $C_{19}H_{15}O_2N_3$ requires C, 55·3; H, 3·9%); *benzoate*, felted needles, m. p. 151°, from $CHCl_3$ (Found : C, 78·5; H, 6·0. $C_{20}H_{19}O_2N$ requires C, 78·7; H, 6·3%); *acetyl* derivative, plates, m. p. 182°, from $Ac_2O$ or MeOH (Found : C, 79·7; H, 6·7. $C_{15}H_{15}ON$ requires C, 80·0; H, 6·7%).

*Benzylidene-4-phenylbenzylamine* (as IV) crystallised from MeOH in pearly plates, m. p. 76° (Found : C, 88·75; H, 6·3%).

Mixtures of 4-phenylbenzaldehyde- and benzaldehyde-*p*-nitrophenylhydrazones melted as follows (A denotes the latter) :

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| A, % | 0 | 14·8 | 25·5 | 30·9 | 39·0 | 47·0 | 65·7 | 75·5 | 82·7 | 100 |
| M. p. | 216° | 203° | 193·5° | 188° | 180° | 172° | 168·5° | 176° | 181° | 190° |

*Interconversion.* (*a*) With 1·45*N*-NaOEt at 85° :

| Isomeride used. | Time at 85° with NaOEt, hr. | Yield, %. | M. p. | Isomeride (IV), %. |
|---|---|---|---|---|
| III | 1 | 95·3 | 180° | 39 |
| IV | 1 | 96 | 180 | 39 |

Equilibrium : IV (39·0%) $\rightleftharpoons$ III (61·0%).

(*b*) With 0·145*N*-NaOEt at 82° :

| Isomeride (III) used. | | | | | Isomeride (IV) used. | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Time at 82° with NaOEt, min. | Yield, %. | M. p. | Isomeride (IV), %. | $k_1 + k_2$, hr.$^{-1}$. | Time at 82° with NaOEt, min. | Yield, %. | M. p. | Isomeride (IV), %. | $k_1 + k_2$, hr.$^{-1}$. |
| 0 | 102 | 216° | 0 | — | 90 | 96 | 180° | 39 | — |
| 5 | 100 | 208·5 | 8·5 | 2·94 | 30 | 99 | 167 | 52 | 3·09 |
| 10 | 100 | 203 | 14·8 | 2·86 | 25 | 98 | 162·5 | 55·5 | 2·86 |
| 15 | 98 | 198·5 | 20 | 2·87 | 20 | — | 164 | 61·5 | 2·99 |
| 20 | 99 | 194·5 | 24 | 2·86 | 15 | 100 | 170·3 | 68 | 2·97 |
| 25 | 97 | 191 | 27·7 | 2·96 | 10 | 100 | 176·3 | 76 | 2·99 |
| 30 | 94·5 | 189·2 | 29·7 | 2·86 | 5 | 101·5 | 181·5 | 83·5 | (3·78) |
| 90 | 95 | 180 | 39 | — | 0 | 100 | 190 | 100 | — |

Equilibrium : IV (39·0%) $\rightleftharpoons$ III (61·0%); $k_1 + k_2$ (mean) = 2·93 hr.$^{-1}$; $k_1/k_2 = 0{\cdot}639$; $k_1 = 1{\cdot}14$; $k_2 = 1{\cdot}79$.

4-*Aminodiphenyl-4′-sulphonic Acid.*—4-Aminodiphenyl (17 g.) was heated with $H_2SO_4$ (30 g.) at 170° for 4 hr., the melt poured into ice-water, and the 4-aminodiphenyl-4′-sulphonic acid (this is the sole product of sulphonation at 130—180°) purified as for sulphanilic acid (Thorpe and Whiteley, "Organic Chemical Analysis," p. 207); yield, 14·5 g. The acid separated from $H_2O$ in iridescent plates, m. p. 270° (eventual decomp.) (Found : C, 58·0; H, 4·5; N, 5·4; S, 12·8. Calc. : C, 57·8; H, 4·5; N, 5·6; S, 12·8%).

*Orientation.*—The Na salt (5·5 g.), suspended in $NaNO_2$ aq. (1·45 g. in 10 c.c. $H_2O$), was slowly treated at 5° with 50% $H_2SO_4$ (40 c.c.); after 2 hr., the colourless diazonium complex was filtered off and washed with EtOH and $Et_2O$; it carbonised suddenly at 161°. The substance and an equal wt. of Zn dust were warmed in dry EtOH (N and acetaldehyde were evolved), and finally the solution was refluxed for 2 hr., filtered, and evaporated in vac. The residue was boiled with 2*N*-$Na_2CO_3$; from the filtered cooled extract, sodium diphenyl-4-sulphonate separated. It was recrystallised from hot $H_2O$, dried at 110°, and heated with $K_4Fe(CN)_6$ (2 parts) in a current of $CO_2$. The distillate consisted of 4-cyanodiphenyl, m. p. 86°, and its polymeride : both were hydrolysed by 50% $H_2SO_4$ containing AcOH to diphenyl-4-carboxylic acid, m. p. and mixed m. p. 220—221°.

### m-*Diphenyl Compounds.*

3-Cyanodiphenyl was prepared by the method of Gomberg and Bachmann (*J. Amer. Chem. Soc.*, 1924, **46**, 2339) or of Gomberg and Pernert (*ibid.*, 1926, **48**, 1372). The tarry product of the coupling reaction from 3-cyanoaniline (75 g.), after removal of excess of $C_6H_6$ was distilled with steam (120°), an ethereal extract of the distillate dried ($CaCl_2$), and the oil in it fractionated : (i) b. p. 100—120°/20 mm. (3 g.), mainly benzonitrile; (ii) b. p. 180—189°/20 mm. (1·5 g.); (iii) b. p. 189—192°/20 mm. (11 g.), consisting of pure 3-cyanodiphenyl, solidified completely, and after crystn. from $Et_2O$–ligroin (b. p. 40—60°) had m. p. 48°. Fraction (ii) became partly solid after seeding, and gave a further small quantity of 3-cyanodiphenyl.

*Diphenyl-3-aldehyde.*—(a) 3-Cyanodiphenyl (11·5 g.) in $Et_2O$ (25 c.c.) was added to $SnCl_2$ (18·5 g.) in $Et_2O$ (150 c.c., saturated with HCl at 0°); after 12 hr., the stannichloride was washed with $Et_2O$ and decomposed with hot $H_2O$.

(b) *Diphenyl-3-carboxyanilide*, prepared by successive treatment of the acid with $SOCl_2$ and $NH_2Ph$ (2 mols.), separated from EtOH in colourless needles, m. p. 184° (Found : C, 83·6; H, 5·6. $C_{19}H_{15}ON$ requires C, 83·5; H, 5·5%). It (9 g.) was heated in $C_2H_2Cl_4$ with $PCl_5$ (7 g.) at 140° for 1 hr., $POCl_3$ and a part of the solvent removed in vac., and the iminochloride added to $SnCl_2$ (30 g.) in $Et_2O$ (250 c.c., saturated with HCl at 0°); after 12 hr., the yellow stannichloride was separated and hydrolysed with 2*N*-HCl (50 c.c.).

The product from (a) or (b) was extracted and roughly dried in $Et_2O$, recovered, and converted into the bisulphite compound, which was colourless after being washed with EtOH and $Et_2O$. Regenerated from the bisulphite compound, *diphenyl-3-aldehyde* had b. p. 187—188°/21 mm. [(a) 4·5 g. : (b) 3 g.] (Found : C, 85·4; H, 5·55. $C_{13}H_{10}O$ requires C, 85·7; H, 5·5%) : *semicarbazone*, needles, m. p. 193°, from EtOH (Found : C, 70·3; H, 5·6. $C_{14}H_{13}ON_3$ requires C, 70·3; H, 5·5%); 2 : 4-*dinitrophenylhydrazone* (prepared according to Brady; J., 1931, 756), orange needles, m. p. 229°, from xylene (Found : C, 63·2; H, 4·0. $C_{19}H_{14}O_4N_4$ requires C, 63·0; H, 3·9%); oxime, a syrup, yielding a hydrochloride, m. p. 118—119°. Oxidation of the aldehyde with $KMnO_4$ and $Na_2CO_3$ gave the acid, m. p. and mixed m. p. 164° (Found : C, 78·8; H, 5·3. Calc. : C, 78·8; H, 5·1%).

3-*Phenylbenzylidenebenzylamine* (as III) was obtained as a faintly yellow oil, b. p. 224°/1 mm. (Found : C, 88·8; H, 6·35. $C_{20}H_{17}N$ requires C, 88·6; H, 6·3%).

3-*Phenylbenzylamine.*—3-Methyldiphenyl was prepared by Gomberg and Pernert's method (*J. Amer. Chem. Soc.*, 1926, **48**, 1372); the fraction (20 g.), b. p. 260—275°, from *m*-toluidine (107 g.) was dissolved in EtOH–HCl and treated with Zn dust to remove azo-compounds, and the product, after evapn. of EtOH, taken up in $Et_2O$, washed with 2*N*-$H_2SO_4$ and 2*N*-$Na_2CO_3$, dried, and distilled in vac.; the hydrocarbon (16 g.) was then obtained as a colourless liquid, b. p. 159—160°/27 mm. By bromination (1 mol. Br) at 195°, ω-bromo-3-methyldiphenyl was obtained as a straw-coloured liquid, b. p. 205—210°/24 mm., which crystallised; twice recryst. from ligroin (b. p. 40—60°), it formed colourless plates (15·5 g.), m. p. 57—58° (Found : C, 62·5; H, 4·5; Br, 33·4. Calc. for $C_{13}H_{11}Br$ : C, 63·1; H, 4·5; Br, 32·4%). [It seems likely that the b. p. 150°/15 mm. given by Ingold and Patel (*J. Indian Chem. Soc.*, 1930, **7**, 107) relates to the hydrocarbon and not the ω-bromo-derivative.] Condensation with potassium phthalimide at 185° afforded *phthalo*-m-*diphenylmethylimide*, needles, m. p. 138°, from EtOH (Found : C, 80·4; H, 4·9; N, 4·4. $C_{21}H_{15}O_2N$ requires C, 80·5; H, 4·8; N, 4·5%), accompanied by a small quantity of phthalimide. Fission with $N_2H_4$ furnished 3-phenylbenzylamine hydrochloride, crystallising from $H_2O$ in colourless plates. The base, b. p. 182°/18 mm., m. p. 29°, formed a *picrate*, yellow needles, m. p. 220° (decomp.), from MeOH (Found : C, 55·2; H, 4·2. $C_{19}H_{16}O_7N_4$ requires C, 55·3; H, 3·9%), and *acetyl* derivative, prisms, m. p. 115—116° (Found : C, 79·8; H, 6·6. $C_{15}H_{15}ON$ requires C, 80·0; H, 6·7%).

*Benzylidene-3-phenylbenzylamine* (as IV), which is hydrolysed by washing in $Et_2O$ with cold 2% AcOH aq., was purified by passage of $CO_2$ through the dry $Et_2O$ solution (cf. J., 1932, 703) : it is a faintly yellow oil, b. p. 220°/1 mm. (Found : C, 88·3; H, 6·4%).

Mixtures of 3-phenylbenzaldehyde- and benzaldehyde-*p*-nitrophenylhydrazones melted as follows (A denotes the latter) :

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| A, % ..................... | 0 | 20·6 | 29·0 | 38·1 | 46·8 | 60·9 | 73·6 | 79·4 | 100 |
| M. p. ..................... | 187·5° | 176° | 170° | 162° | 150·5° | 166·5° | 176·5° | 180° | 190° |

*Interconversion.* (*a*) With 1·45*N*-NaOEt at 85° :

| Isomeride used. | Time at 85° with NaOEt, hr. | Yield, %. | M. p. | Isomeride (IV), %. |
|---|---|---|---|---|
| III | 1 | 95 | 155° | 44 |
| IV | 1·5 | 95 | 155* | 44 |
|  | 1·75 | 95 | 155 | 44 |

* To 4·5 mg. of this equilibrium specimen, 2·0 mg. of *m*-phenylbenzaldehyde-*p*-nitrophenylhydrazone were added; the mixture had m. p. 167·5° : calc., 168°.

Equilibrium : IV (44·0%) $\rightleftharpoons$ III (56·0%).

(*b*) With 0·145*N*-NaOEt at 82° :

| Isomeride used. | Time at 82° with NaOEt, min. | Yield, %. | M. p. | Isomeride (IV), %. | $k_1 + k_2$, hr.$^{-1}$. Calc. from zero time. | Calc. by time diff. |
|---|---|---|---|---|---|---|
| III | 0 | 101·5 | 187·5° | 0 | — | — |
|  | 10 | 100·5 | 181 | 13 | 2·10 | — |
|  | 12·5 | 99 | 178·2 | 17 | 2·34 | — |
|  | 15 | 100 | 177 | 19 | 2·76 | — |
|  | 17·5 | 100 | 175·7 | 21 | 2·22 | — |
|  | 20 | 98·5 | 174 | 23·5 | 2·28 | — |
|  | 22·5 | 99 | 172·5 | 25·5 | 2·30 | — |
|  | 25 | 96 | 172 | 26 | 2·14 | — |
|  | 27·5 | 98 | 170·5 | 28 | 2·21 | — |
|  | 30 | 98 | 169 | 29·5 | 2·22 | — |
|  | 35 | 98 | 168 | 31·5 | 2·18 | — |
|  | 90 | 95 | 155 | 44 | — | — |
| IV | 90 | 95 | 155 | 44 | — | — |
|  | 35 | 100 | 162 | 57 | 2·50 | 2·26 |
|  | 30 | 99 | 164·7 | 59·7 | 2·54 | 2·18 |
|  | 25·5 | 98 | 168 | 62·5 | 2·59 | 2·13 |
|  | 20 | 99 | 171·5 | 67·5 | 2·73 | (1·74) |
|  | 15 | 100 | 174 | 70·0 | (3·06) | 2·11 |
|  | 10 | (102) | 177·2 | 75·0 | (3·52) | (3·52) |
|  | 0 | 100 | 190 | 100 | — | — |

The average value of the constant $k_1 + k_2$ (calc. from zero time) for both (III) and (IV) is 2·33 hr.$^{-1}$, and that similarly calc. for (III) only is 2·22 hr.$^{-1}$; the average of the values for (III) and those calc. by time differences for (IV) is 2·21 hr.$^{-1}$.

Equilibrium : IV (44·0%) $\rightleftharpoons$ III (56·0%); $k_1 + k_2$ (mean) = 2·33 hr.$^{-1}$; $k_1/k_2 = 0·785$; $k_1 = 1·02$; $k_2 = 1·31$.

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