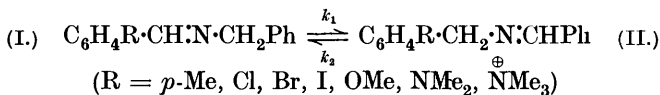# CLXIII.—*Symmetrical Triad Prototropic Systems. Part VII. The Analogy between Symmetrical Triad Systems and Aromatic Side-chain Reactivity, and the Effect of p-Substitution on Mobility and Equilibrium in the αγ-Diphenylmethyleneazomethine System.*

By Charles William Shoppee.

THE present paper describes the investigation (see Shoppee, J., 1930, 968) of the effect of substitution on mobility and equilibrium in the methyleneazomethine system (I $\rightleftharpoons$ II).

$$(\text{I.}) \quad C_6H_4R\cdot CH\dot{:}N\cdot CH_2Ph \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_6H_4R\cdot CH_2\cdot N\dot{:}CHPh \quad (\text{II.})$$

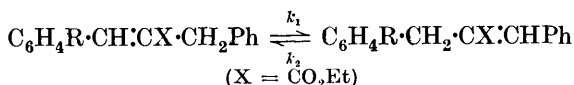$$(R = p\text{-Me, Cl, Br, I, OMe, NMe}_2, \overset{\oplus}{N}Me_3)$$

Substitution and Mobility.—Tautomeric systems activated by one or more aromatic residues may be regarded as exemplifying aromatic side-chain reactivity; prototropic systems, such as propenylbenzene $\rightleftharpoons$ allylbenzene or that formulated above, correspond to side-chain transformations requiring electron recession from the side-chain (Ingold and Rothstein's type B, J., 1928, 1217), and, conversely, anionotropic systems, *e.g.*, cinnamyl alcohol $\rightleftharpoons$ α-phenylallyl alcohol, are analogous to side-chain reactions requiring electron accession (type A, *loc. cit.*). The analogy drawn by Ingold and Patel (*J. Indian Chem. Soc.*, 1930, 95) between aromatic hydrogen substitution and side-chain reactivity of type A, and between anionic aromatic replacements and side-chain reactivity of type B, may therefore be extended to simple anionotropic and prototropic systems respectively. Hence facilitation by nuclear substituents of (i) anionic aromatic replacements, (ii) side-chain reactivity of type B, and (iii) prototropy in systems activated by aromatic groups should run generally parallel.

The velocity coefficients for the alkaline hydrolysis of *p*-substituted ethyl benzoates (Kindler, *Annalen*, 1926, **150**, 1), which is a reaction of type B, show that the order of facilitation by substituents is

S S

$NR_2 < OMe < Me < Hals.$; the effect of R on the velocity of interconversion of the isomerides (I, II) under constant conditions of temperature and catalysis is as follows :

p-Substituent R.	NMe$_2$.	Me.	OMe.	I.	Br.	Cl.
$k_1 + k_2$ (hr.$^{-1}$)	0·054	0·322	0·557	6·82	7·09	7·83
Dipole moment of $C_6H_5 \cdot R$ (E.S.U. $\times$ 10^{-18})	1·39	0·50	$-0·80$	$-1·25$	$-1·51$	$-1·56$

For the facilitation of prototropy in the simple three-carbon system,

$$C_6H_4R \cdot CH \vdots CX \cdot CH_2Ph \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_6H_4R \cdot CH_2 \cdot CX \vdots CHPh$$
$$(X = CO_2Et)$$

the sequence p-NMe$_2 < p$-Me, p-OMe $< p$-Hals. has already been found (Shoppee, *loc. cit.*), and it is now seen that the same sequence, p-NMe$_2 < p$-Me $< p$-OMe $< p$-Hals., expresses the behaviour of the methyleneazomethine system.

With regard to the above table, the previous conclusion that the velocities of interconversion of simple triad tautomerides follow strictly and without exception the order of the dipole moment is confirmed, showing .that mobility in such systems is dependent solely on the facilitation of ionisation.

In contrast with the foregoing, Kindler's series does not follow the order of dipole moments, the methoxyl group which attracts electrons taking a position between the methyl and the dimethylamino-group, the permanent moments of which are in the opposite direction to that of methoxyl. This difference between Kindler's data and the present results, combined with the circumstance that both the reaction which he studied and that considered here are aromatic side-chain reactions of type B, illustrates the author's criticism (*loc. cit.*) in another connexion against the carrying over of a polar influence from one reaction to another without regard to the substances which control the part played by the tautomeric effect in each. When this is considered, the cause of the difference between Kindler's series and that illustrated in the preceding table becomes apparent : in Kindler's compounds there exists in the p-position to the variable nuclear substituent a carboxyl (or cyano-) group, the tautomeric polarisation of which plays a necessary part in the reaction; if, therefore, the variable substituent exerts a $+ T$ effect, that will act in such a way as to detract from the effective $- T$ polarisation of the carboxyl group. In the paper already cited, it was pointed out that the tautomeric effect of a group can only operate against the progress of a reaction if there is also present a facilitating tautomeric effect from which the former effect can be treated as subtractable ; now that is the case in Kindler's reactions,

and it explains the position of the methoxyl group. No such conditions prevail in the simple triad tautomeric systems, wherefore the potential $+ T$ effect of substituents does not disturb the normal sequence based on dipole moments.

Substitution and Equilibrium.—In a *simple* triad prototropic system, since only carbon atoms are available as seats for the anionic charge, it would appear that equilibrium would be controlled solely by the relative stability of the electromeric forms of the ion (compare *Ann. Reports*, 1927, **24**, 106).

At first sight this would seem to suggest that the relative permanence of that form of the ion, which on combination with a proton would give isomeride (I), would diminish as the electron affinity of R decreases (from $- I$ to $+ I$). On the other hand, equilibria relating to the simple three-carbon system have already been recorded (Shoppee, *loc. cit.*) which show that such a simple view cannot be maintained. The anomaly may be described in the statement that interpenetrating a series of $\pm I$ groups, which amongst themselves are correctly arranged, a series of $- I + T$ groups is found in which the expected order is completely inverted. The following table shows that the methyleneazomethine system exhibits precisely the same relations in its equilibria. The groups NMe_2, OMe, I, Br, Cl, which are capable of a tautomeric effect ($+ T$), form amongst themselves a continuous polar sequence which interpenetrates the sequence formed by groups Me, H, $\overset{\oplus}{N}Me_3$, which are incapable of tautomeric polar activity; but the NMe_2-end of the former sequence points to the $\overset{\oplus}{N}Me_3$-end of the latter.

p·Substituent, R.	$\overset{\oplus}{N}Me_3$.	NMe₂.	OMe.	I.	(H).	Br.	Cl.	Me.
K	—	0·149	0·370	0·887	1·00	1·08	1·13	1·22
Isomeride (I), %	—	87·0	73·0	53·0	50·0	48·0	47·0	45·0

Having regard to these results and those previously recorded, it becomes abundantly evident that the simple view, indicated above, of the influence of substitution on equilibrium is quite inadequate, and that a more thorough theoretical treatment is required.

Consider the tautomeric system

$$A \underset{v_2}{\overset{v_1}{\rightleftharpoons}} \text{Ion} \underset{v_4}{\overset{v_3}{\rightleftharpoons}} A'$$
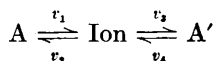
If the concentration of the intermediate ion is small, then

$$K = \frac{v_1}{v_2} \cdot \frac{v_3}{v_4} = \frac{v_1}{v_4} \bigg/ \frac{v_2}{v_3}$$

that is, the equilibrium constant is measured by the ratio of the
ratio of the rates of ionic dissociation of the two forms to the ratio
of their rates of ionic association. Ionic dissociation of hydrogen,
which is analogous to side-chain reactivity of type B (*vide supra*), is
facilitated by effects $- I$ and $- T$, and retarded by effect $+ I$ only;
similarly, the ionic reassociation of hydrogen, being analogous to
side-chain reactivity of type A, is facilitated by effects $+ I$ and
$+ T$, and retarded by effect $- I$ only. Hence equilibrium (as
opposed to mobility) involves two rate-affecting phases which partake
of the nature of side-chain reactions of opposite types. Theoretical

FIG. 1.
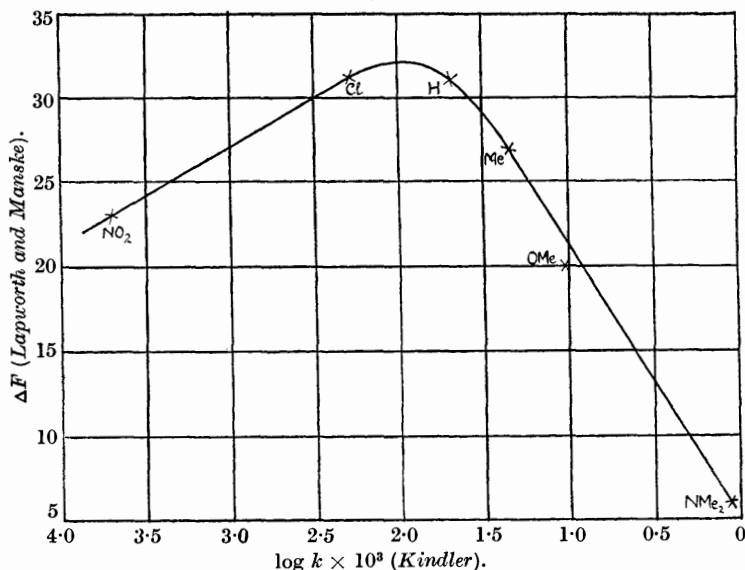
provision for side-chain reactions of such composite type has already
been made (Ingold and Patel, *loc. cit.*), and for their recognition a
practical criterion has been given, which, in its application to
equilibria, is that the equilibrium constant K may be altered in the
same direction by substituents of either polar type according to
their strength.

It has been suggested that such composite conditions prevail in
the formation of cyanohydrins (Ingold, *Ann. Reports*, 1928, **25**, 147),
$C_6H_4R \cdot CH \vdots O + HCN \rightleftharpoons C_6H_4R \cdot CH(OH) \cdot CN$, and the effect of
substitution on equilibrium in this system has been studied by
Lapworth and Manske (J., 1928, 2533). Their results, expressed as
energy differences (ΔF) proportional to log K, yield a sequence

which, although not identical with the velocity sequence obtained by Kindler, may be compared therewith in view of the similarity of the structures and reactions involved; and the comparison shows that the relation is of this kind, namely, that Lapworth and Manske's series is Kindler's series doubled back upon itself at a certain inter-mediate point. If Lapworth and Manske's energy differences are plotted against Kindler's velocity coefficients or their logarithms for corresponding substituents, a curve possessing a single maximum is

FIG. 2.

——— *Methyleneazomethine system.*
– – – *Simple three-carbon system.*
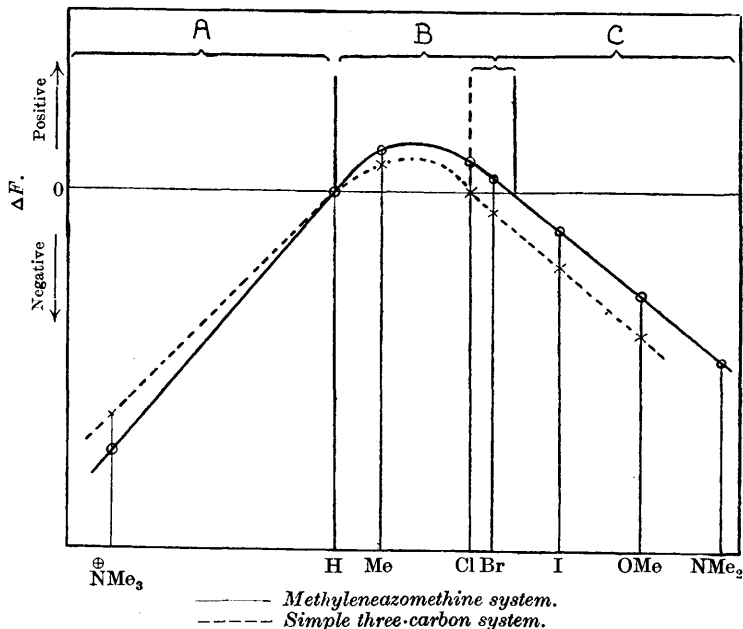
obtained (Fig. 1), substituents of opposite polar type (*e.g.*, NO_2, Me) altering log K in the same direction.

Consideration shows that the equilibrium constants given above for the methyleneazomethine system and those previously recorded for the simple three-carbon system are susceptible of an entirely similar analysis; but the reference series is not Kindler's: it is the series which expresses the order in which groups in competition would control ordinary nuclear aromatic substitution, *viz.*, $\overset{\oplus}{N}Me_3$, H, Cl, Br, I, OMe, NMe_2. Although complete data do not exist for the relative *op*-directive powers of these groups, the relation between the series and those given by the equilibria of the simple three-carbon and

methyleneazomethine triad systems may be made clear by means of a symbolic diagram (Fig. 2). If we arrange the aromatic substitution series in the right order at arbitrary intervals along the horizontal axis, and set up ordinates corresponding to the determined values of ΔF we obtain for each tautomeric system a curve with a single maximum entirely similar to that given by the analogous comparison of cyanohydrin equilibria with the speeds of hydrolysis of benzoic esters.

It follows that the explanation given to Lapworth and Manske's results, *viz.*, the co-existence of two antagonistic processes of control, can be applied in the cases now under consideration. Furthermore, it follows that the two opposing processes must be such that the analogy between the reaction for which Lapworth and Manske measured the equilibrium and that for which Kindler measured the velocity is paralleled by an analogy between the factors controlling equilibria and those determining orientation in aromatic hydrogen substitution.

Now the most striking characteristic of the ordinary orientation series, and the property which distinguishes it from the various series relating to aromatic side-chain reactivity and nuclear anionic replacement, is the very great importance of the $+ T$ effect, as illustrated by the *op*-orientation of electron-attracting chlorine. That this series provides the basis to which the new results may be referred shows that the processes of duplex control must relate to a stage in the chemical reaction in which the $+ T$ effect can be operative, *i.e.*, to a stage in which the external reagent is electron-seeking. This shows that it is not the ionisation process but the reassociation stage of the isomeric change which is fundamentally important in controlling the equilibrium, and the equilibria are thereby strongly distinguished from the mobilities. Examination of the curve (Fig. 2) shows that this conclusion is definite for sections B and C in which *op*-directing groups of the types $+ I$, $+ I + T$, and $- I + T$ are interspersed in the manner characteristic of the orientation series, although it might require modification in its application to section A, were that filled in by other *m*-directing groups. In short, the present conclusion is that disparity between rates of ionic reassociation controls K, certainly in sections B and C, and possibly in section A; but further work is projected to decide whether in the presence of *m*-directing groups disparity between rates of ionisation may exert an appreciable effect on the equilibrium constant. With this reservation, we proceed on the assumption that the conclusion concerning the stage at which the duplex mechanism enters is at least a large part of the truth.

It is necessary therefore to consider how constitutional influences may affect the location of the charge on the electromeric ion (III). In this ion the anionic charge is distributed between C_α and C_γ,

$$R-\langle\rangle-\overset{\ominus}{\overline{CH-N-CH}}-\langle\rangle \quad \text{(III)}.$$
$$\phantom{R-\langle\rangle-}\alpha\gamma$$
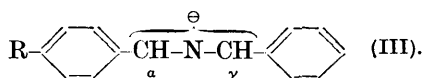
but a part of this charge resides in all probability in the aromatic rings. First, if R attracts electrons the part of the charge situated at C_α may become largely absorbed in the aromatic ring $R \cdot C_6H_4-$, wherefore recombination will happen mainly at C_γ. Secondly, suppose R strongly repels electrons or releases them easily when a proton or a polarised electron-seeking alcohol molecule $(\delta +)H-OEt(\delta -)$ enters the neighbourhood of the methyleneazomethine system; then if that effect is strong enough, the charge developed on the carbon atom para to R may repel electrons from C_α to C_γ and again produce predominating combination at C_γ. Thirdly, suppose that R repels electrons slightly or releases them slightly under the conditions obtaining just prior to reassociation : there might then arise a condition in which the tendency of the aromatic ring to absorb the charge at C_α is frustrated, but yet the polarisation caused by R is not strong enough to repel the anionic charge from C_α to C_γ. Predominating combination will then occur at C_α, since the unsubstituted aromatic ring will still absorb the charge at C_γ. The foregoing describes in order the cases of $\overset{\oplus}{N}Me_3$, NMe_2, and either Me or Cl; and, generally, the cases expressed by the parts of the curve indicated in Fig. 2 by the letters A, C, and B, respectively.

EXPERIMENTAL.

Preparation of Azomethines.—The azomethines were obtained by condensation of the appropriate aldehyde with a slight excess of the requisite amine at 100° for $\frac{1}{4}$ hour; an ethereal solution of the product was washed with 2% aqueous acetic acid, sodium hydrogen carbonate, and water, dried with potassium carbonate, and the ether evaporated. The azomethines tend to decompose on keeping, and it is essential to recrystallise them immediately before use.

Interconversion.—The standard conditions employed for interconversion of all azomethines were : catalyst, $0 \cdot 145N$-alcoholic sodium ethoxide; temperature, 82°. The product was isolated by addition of water and extraction with ether (twice); the ethereal extract was washed with water, dried with potassium carbonate, and evaporated.

Determination of Mobility and Equilibrium.—Preliminary experiments with individual azomethines and artificial mixtures led to a general method whereby their proportions could be estimated with some accuracy. The method depends upon the discovery (compare von Auwers and Müller, *Ber.*, 1917, **50**, 1149) that azomethines undergo fission quantitatively, when treated with excess of a hydrazine acetate, to give the appropriate aldehyde-hydrazone and the complementary benzylamine. *p*-Nitrophenylhydrazine was chosen as giving hydrazones possessing considerable insolubility but melting without decomposition, and the following procedure was adopted. The mixed azomethines were dissolved in hot glacial acetic acid (2·5 c.c.), and a hot filtered solution of *p*-nitrophenylhydrazine (2 mols.) in 50% acetic acid (5 c.c.) was added; after a few minutes' warming on the steam-bath, water (42·5 c.c.) was added, giving a 10% acetic acid solution (compare Thorpe and Whiteley, " Organic Chemical Analysis," p. 187). After some hours, the precipitate was collected on a weighed Gooch crucible, washed with 10% acetic acid* until the washings gave only a faint colour with sodium hydroxide, and dried at 110°. After being weighed, portions of the precipitate were analysed thermally. The *p*-nitrophenylhydrazones so obtained from individual azomethines were practically pure and were used for the construction of temperature–composition diagrams without purification. All such diagrams were of the two-branch type, and the products of the interconversion experiments were strictly binary in character. All m. p.'s given are uncorrected, but were determined under identical conditions in the same apparatus.

In the course of this work, the following *p*-substituted benzaldehyde-*p*-nitrophenylhydrazones have been obtained :

	M. p.	Found. C, %.	H, %.	Calc. C, %.	H, %.
p-*Chloro-*	216·5°	56·5	4·0	56·7	3·7
p-*Bromo·*	205·5	49·1	3·6	48·8	3·2
p-*Iodo-*	201	42·7	2·8	42·5	2·75
p-*Methoxy·*	161	61·5	5·1	61·9	4·9
p-*Acetamido·*	262	60·4	4·9	60·4	4·7
p-*Dimethylamino-*	182	63·2	5·7	63·4	5·7
p-*Methyl*	196·5	—	—	—	—
p-*Nitro·*	249	—	—	—	—

p-*Dimethylaminobenzaldehyde*-p-*bromophenylhydrazone* has m. p. 181° (decomp.) (Found : C, 56·6 ; H, 5·2. $C_{15}H_{16}N_3Br$ requires C, 56·6 ; H, 5·1%).

Chloro-compounds.—p-*Chlorobenzylidenebenzylamine* (as I) separ-

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* p-Dimethylaminobenzaldehyde-*p*-nitrophenylhydrazone is slightly soluble in 10% acetic acid, and prolonged washing must be avoided.

ates from ligroin (b. p. 40—60°) or dilute methyl alcohol with cooling, in long, colourless needles, m. p. 34° (Found : C, 73·5; H, 5·4. $C_{14}H_{12}NCl$ requires C, 73·4; H, 5·3%).

p-*Chlorobenzylamine.* Potassium phthalimide (46 g.) and p-chlorobenzyl bromide (51 g.) were heated together at 180° for 2 hours, and the solid obtained by cooling was extracted with boiling glacial acetic acid, from which p-*chlorobenzylphthalimide* crystallised in colourless needles, m. p. 124° (57 g.) (Found : C, 66·1; H, 3·5. $C_{15}H_{10}O_2NCl$ requires C, 66·3; H, 3·7%). By treatment with half its weight of sodium hydroxide in 10% solution (boiling for 0·5 hr.) and acidification, the imide is converted quantitatively into p-*chlorobenzylphthalamic acid,* which separates from alcohol in needles, m. p. 185° (Found : C, 61·2; H, 4·1. $C_{15}H_{12}O_3NCl$ requires C, 62·2; H, 4·1%). The crude amic acid by hydrolysis for 24 hours with three parts of 20% hydrochloric acid yields phthalic acid and the hydrochloride of the base, m. p. 242—243° (12 g.), from which p-chlorobenzylamine is readily obtained as a colourless liquid, b. p. 108—109°/14 mm., which combines with carbon dioxide with great rapidity giving the carbonate, m. p. 118—119°. The *picrate,* crystallised from dilute methyl alcohol, has m. p. 210—211° (decomp.) (Found : C, 42·2; H, 3·4. $C_{13}H_{11}O_7N_4Cl$ requires C, 42·1; H, 3·0%). The *benzoate* separates from chloroform–ligroin (b. p. 60—80°) in pearly plates, m. p. 155—156° (Found : C, 63·8; H, 5·3. $C_{14}H_{14}O_2NCl$ requires C, 63·8; H, 5·3%); the acetyl derivative, needles from ligroin (b. p. 80—100°), has m. p. 106—107°.

Benzylidene-p-*chlorobenzylamine* (as II) crystallises from cooled ligroin (b. p. 40—60°) in long needles, m. p. 36—37° (Found : C, 73·2; H, 5·3. $C_{14}H_{12}NCl$ requires C, 73·4; H, 5·3%). Mixtures of the p-nitrophenylhydrazones of p-chlorobenzaldehyde and benzaldehyde (A) melted as follows, the percentages being those of the latter nitrophenylhydrazone.

A, %	0	20·3	39·0	42·6	47·6	53·5	60·5	65·6	79·8	100
M.p.	216·5°	204·5°	192°	190°	186°	181°	174°	171·5	179°	190°

Interconversion by $1·45N$-*sodium ethoxide at* 85°.

Isomeride used.	Time at 85° with NaOEt (hrs.).	Yield, %.	M. p.	Isomeride (II), %.
$C_6H_4Cl·CH:N·CH_2Ph$ (I)	0	99·8	216·5°	0
	1·0	96	181·5	
	2·0	93	181·5	
$C_6H_4Cl·CH_2·N:CHPh$ (II)	0·75	94	181·5	53
	0·50	95	181·0	
	0·25	95	181·5	
	0	100·0	190·0	100

Equilibrium : II (53·0) ⇌ I (47·0).

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Interconversion by 0·145N-*sodium ethoxide at* 82°.

Isomeride used.	Time at 82° with NaOEt (mins.).	Yield, %.	M. p.	Isomeride (II), %.	$k_1 + k_2$ (hrs.$^{-1}$).
I	0	99·8	216·5°	0	—
	5	98	201·5	25·5	7·86
	10	93	192·5	38·5	7·77
	15	95	187·5	45·5	7·81
	30	94	181·5	53·0	—
II	30	94	181·5	53·0	—
	15	93	172·0	62·0	(6·60)
	10	95	171·5	65·5	7·93
	5	94	177·5	77·5	7·81
	0	100·0	190·0	100·0	—

Equilibrium : II (53·0) $\rightleftharpoons$ I (47·0); $k_1 + k_2$ (mean) = 7·83 hr.$^{-1}$; $k_1/k_2 = 1·128$; $k_1 = 4·14$; $k_2 = 3·69$.

Bromo-compounds.—p-*Bromobenzylidenebenzylamine* (as I) forms colourless needles from dilute alcohol (with cooling), m. p. 43° (Found : C, 61·6; H, 4·5. $C_{14}H_{12}NBr$ requires C, 61·3; H, 4·4%).

p-*Bromobenzylamine.* Potassium phthalimide (37 g.) and p-bromo-benzyl bromide (50 g.), heated together for 2 hrs. at 180—200°, furnish p-*bromobenzylphthalimide*, which separates from glacial acetic acid in colourless needles, m. p. 133° (52 g.) (Found : C, 56·9; H, 3·1. $C_{15}H_{10}O_2NBr$ requires C, 57·0; H, 3·2%). By treatment with hot 2N-sodium hydroxide for 0·5 hr. and acidification of the warm solution, p-*bromobenzylphthalamic acid*, m. p. 185° after crystallisation from alcohol, is obtained in quantitative yield (Found : C, 54·2; H, 3·7. $C_{15}H_{12}O_3NBr$ requires C, 53·9; H, 3·6%). Hydrolysis of the amic acid with 3 parts of concentrated hydrochloric acid and 1 part of alcohol was slow, and incomplete after 24 hours; evaporation of the solution after removal of phthalic acid and unchanged imide gave 12 g. of p-bromobenzylamine hydrochloride, from which the base, b. p. 118—119°/10 mm., m. p. 25—25·5°, was obtained as usual. The *picrate* (from methyl alcohol) has m. p. 221° (Found : C, 37·7; H, 2·8. $C_{13}H_{11}O_7N_4Br$ requires C, 37·6; H, 2·7%). The *benzoate* separates from chloroform–ligroin (b. p. 60—80°) in iridescent plates, m. p. 162° (Found : C, 54·9; H, 4·7. $C_{14}H_{14}O_2NBr$ requires C, 54·5; H, 4·67%). The *acetyl* derivative crystallised from ligroin (b. p. 80—100°) has m. p. 113° (Found : C, 47·2; H, 4·4. $C_9H_{10}ONBr$ requires C, 47·4; H, 4·3%).

*Benzylidene·*p-*bromobenzylamine* (as II) separates from dilute methyl alcohol in long colourless needles, m. p. 54·5° (Found : C, 61·3; H, 4·5. $C_{14}H_{12}NBr$ requires C, 61·3; H, 4·4%).

Mixtures of p-bromobenzaldehyde- and benzaldehyde-p-nitro-phenylhydrazones melted as follows (A denotes the latter) :

A, %	0	22·9	40·0	47·5	52·3	55·0	65·3	76·0	100·0
M.p.	205·5°	188·0°	175·0°	169·5°	166·0°	164·5°	170·5°	176·0°	190·0°

Interconversion.—(a) With 1·45N-sodium ethoxide at 85°, either

azomethine after treatment for 1 hr. yielded a mixture of p-nitro-phenylhydrazones, m. p. 165°, corresponding with an equilibrium ratio II (52) $\rightleftharpoons$ I (48). (b) With $0.145N$-sodium ethoxide at 82° :

Isomeride used.	Time with NaOEt (mins.).	Yield, %.	M. p.	Isomeride (II), %.	$k_1 + k_2$ (hrs.$^{-1}$).
	0	99·7	205·5°	0	—
	2·5	99	196·0	13	6·89
	4	98	192·0	19	6·80
	5	99	187·0	24	7·42
	6	97	185·0	26·5	7·11
I	8	98	182·5	31·5	6·97
	10	96	177·5	37	7·45
	12	—	171·5	45	—
	20	94	165·0	52	—
	30	—	165·0	52	—
	45	95	165·0	52	—
	45	—	165·0	52	—
	12	98	166·0	58	(10·4)
	10	98	171·0	67	6·97
II	7·5	98	173·5	72	6·99
	5	98·5	177·5	78·5	7·12
	2·5	99	182·5	87·5	7·24
	0	100	190·0	100	—

Equilibrium : II (52) $\rightleftharpoons$ I (48); $k_1 + k_2$ (mean) $= 7.09$ hrs.$^{-1}$; $k_1/k_2 = 1.083$; $k_1 = 3.69$; $k_2 = 3.40$.

Iodo-compounds.—p-*Iodobenzylidenebenzylamine* (as I). p-Iodo-benzaldehyde, obtained in 80% yield by oxidation of p-iodobenzyl bromide with copper nitrate solution, condenses with benzylamine to give the *azomethine*, which forms needles from methyl alcohol after two crystallisations, m. p. 56° (Found : C, 51·7; H, 3·5. $C_{14}H_{12}NI$ requires C, 52·3; H, 3·8%).

p-*Iodobenzylamine.* p-Iodobenzyl bromide and potassium phthal-imide at 180—190° afford 70% of p-*iodobenzylphthalimide*, m. p. 137° after crystallisation from glacial acetic acid (Found : C, 49·7; H, 2·8. $C_{15}H_{10}O_2NI$ requires C, 49·6; H, 2·8%), which is converted quantitatively by hot 10% sodium hydroxide into p-*iodobenzyl-phthalamic acid*, m. p. 185°, after crystallisation from dilute alcohol (Found : C, 47·3; H, 3·3. $C_{15}H_{12}O_3NI$ requires C, 47·25; H, 3·2%). This resists hydrolysis by hydriodic–acetic acid, and hydrochloric acid at 190° yields mainly benzylamine. The base was therefore prepared by iodination of acetbenzylamide (m. p. 60—61° *), obtained by Amsel and Hoffman's method (*Ber.*, 1886, **19**, 1286); this amide was treated with a 10% excess of iodine monochloride in glacial acetic acid at 100° for 1 hour and kept over-night. After dilution, ether extraction, washing with sodium carbonate followed by sodium thiosulphate, and evaporation, the product was steam-distilled for 2 hours to remove traces of the o-isomeride and any

* Goss, Ingold, and Wilson (*J.*, 1926, 2459) give m. p. 133° in error; this figure refers to acet-p-nitrobenzylamide.

unchanged acetbenzylamide. The crude *p*-isomeride separated when the contents of the distilling flask were cooled, and was filtered off and crystallised repeatedly from dilute acetic acid or dilute alcohol; *acet*-p-*iodobenzylamide* forms colourless needles, m. p. 132° (Found : C, 39·3; H, 3·75; I, 45·5. $C_9H_{10}ONI$ requires C, 39·3; H, 3·7; I, 46·2%), and by hydrolysis with aqueous-alcoholic 10% sodium hydroxide affords *p*-iodobenzylamine, m. p. 45°, the *picrate* of which separates from methyl alcohol in rhombic prisms, m. p. 231° (decomp.) (Found : C, 33·7; H, 2·5. $C_{13}H_{11}O_7N_4I$ requires C, 33·7; H, 2·6%).

Benzylidene-p-*iodobenzylamine* (as II) crystallises from methyl alcohol in needles, m. p. 58·5° (Found : C, 52·5; H, 3·8. $C_{14}H_{12}NI$ requires C, 52·3; H, 3·8%).

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

A, %	0	18·8	35·5	40·0	46·0	48·0	50·0	54·5	60·0	78·0	100
M.p.	201°	184°	168°	163°	157°	155°	157°	163°	167·5°	178°	190°

Interconversion. (*a*) With 1·45N-sodium ethoxide at 85°, either azomethine after treatment for 1 hour yielded a mixture of *p*-nitrophenylhydrazones, m. p. 156°, corresponding with an equilibrium ratio II (47) $\rightleftharpoons$ I (53). (*b*) With 0·145N-sodium ethoxide at 82° :

Isomeride used.	Time with NaOEt (mins.).	Yield, %.	M. p.	Isomeride, II, %.	$k_1 + k_2$ (hrs.$^{-1}$).
	0	100·5	201°	0	—
	2	93	192	10	6·83
	4	92	185	17·5	6·61
I	6	—	180	23	6·32
	8	92	175·5	28	6·35
	10	93·5	171	32·5	6·52
	60	95	156 *	47	—
	60	94	155·5	47	—
	10	94	168·5	62	7·17
II	6	95	175	73·5	6·89
	3	97	181	84	6·82
	0	100	190	100	—

Equilibrium: II (47) $\rightleftharpoons$ I (53); $k_1 + k_2$ (mean) = 6·82 hr.$^{-1}$; $k_1/k_2 = 0·887$; $k_1 = 3·20$; $k_2 = 3·62$.

* The eutectic mixture, m. p. 155°, consists of 48% II + 52% I; a mixture of 12·3 mg. of the equilibrium specimen and 5·1 mg. of *p*-iodobenzaldehyde-*p*-nitrophenylhydrazone melted at 166·5° (Calc. for 47% of II: 166·5°).

Methoxy-compounds.—The methoxy-azomethines were prepared as already described (Ingold and Shoppee, J., 1929, 1202).

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

A, %	0	21·5	39·0	51·2	59·9	70·3	76·8	80·0	100
M. p.	161°	151°	143°	149·5°	160°	168°	174°	176°	190°

Interconversion by 1·45N-*sodium ethoxide at* 85°. The azomethine (I) after treatment for 1 hour yielded a mixture of *p*-nitrophenyl-

hydrazones, m. p. 148·5°, raised by admixture with p-anisaldehyde-p-nitrophenylhydrazone to 151·5° (calc., 151·5°); it therefore contained 73% of the last-named, corresponding with an equilibrium ratio II (27·0) $\rightleftharpoons$ I (73·0). The value found previously (*loc. cit.*) was II (21) $\rightleftharpoons$ I (79).

Interconversion by 0·145N-sodium ethoxide at 82°.

Isomeride used.	Weight taken.	Time with NaOEt, hrs.	Yield, %.	M. p.	Isomeride (II), %.	$k_1 + k_2$ (hrs.$^{-1}$).
	⎧ 0·100	0	100	161·0°	0	—
	⎪ 0·100	0·5	97	158·0	6·5	0·548
	⎪ 0·100	0·75	99	157·0	9·0	0·540
I	⎨ 0·100	1·0	99	155·7	11·5	0·553
	⎪ 0·100	2·0	94	153·0	18·0	0·548
	⎪ 0·100	3·0	98	152·0	20·0	0·585
	⎩ 0·100	5·0	97	148·5	23·0	—
	⎧ 0·102	6·0	96	148·5	23·0	—
	⎪ —	3·0	—	143·0	39·0	0·601
	⎪ 0·109	2·0	95	147·5	49·5	0·576
II	⎨ 0·104	1·25	97	161·0	62·0	0·624
	⎪ 0·119	0·75	91	174·0	76·8	(0·359)
	⎪ 0·105	0·5	95	180·0	85·0	0·484
	⎩ 0·100	0	100	190·0	100·0	—

Equilibrium : II (27·0)$\rightleftharpoons$I (73·0); $k_1 + k_2$ (mean) = 0·557 hrs.$^{-1}$; $k_1/k_2 = 0·369$; $k_1 = 0·150$; $k_2 = 0·407$.

Dimethylamino - compounds. —p - *Dimethylaminobenzylidenebenzyl - amine* (as I) separates from ligroin (b. p. 60—80°) in clusters of yellow prisms, m. p. 75°, b. p. 248°/18 mm. ; admixture with cuprous chloride (compare Haas, J., 1906, **89**, 570) is necessary to obtain a satisfactory analysis (Found : C, 80·0; H, 7·9; N, 12·4. $C_{16}H_{18}N_2$ requires C, 80·6; H, 7·6; N, 11·8%). The azomethine is readily soluble in 2N-acetic acid and is precipitated unchanged by alkali.

p-*Dimethylaminobenzylamine.* p-Dimethylaminobenzaldoxime was prepared by the method given by Bamberger and Scheutz (*Ber.,* 1901, **34**, 2024) for p-anisaldoxime, and melted at 148° (compare Bresler, Friedemann, and Mai, *Annalen,* 1907, **353**, 234). Reduction in 5 g. portions with 3% sodium amalgam in the presence of acetic acid afforded the *base* as a water-clear liquid, b. p. 158—159°/25 mm. It yields two picrates, the *monopicrate,* red needles from methyl alcohol, m. p. 187—189° (decomp.) (Found : C, 47·1; H, 4·5. $C_{15}H_{17}O_7N_5$ requires C, 47·5; H, 4·5%), and the *dipicrate,* yellow needles from methyl alcohol, m. p. 179—180° (decomp.) (Found : C, 41·8; H, 3·4. $C_{21}H_{20}O_{14}N_8$ requires C, 41·5; H, 3·3%). The *acetyl* derivative crystallises from ligroin (b. p. 60—80°) in needles, m. p. 79° (Found : C, 69·1; H, 8·3. $C_{11}H_{16}ON_2$ requires C, 68·8; H, 8·4%), and the *benzoate* separates from chloroform–ligroin in needles, m. p. 156·5° (Found : C, 70·4; H, 7·6. $C_{16}H_{20}O_2N_2$ requires C, 70·5; H, 7·4%).

*Benzylidene-*p-*dimethylaminobenzylamine* (as II) forms pale yellow

prisms, m. p. 57°, after two crystallisations from ligroin (b. p. 40—60°) (Found : C, 80·8; H, 7·7. $C_{16}H_{18}N_2$ requires C, 80·6; H, 7·6%).

Mixtures of p-dimethylaminobenzaldehyde- and benzaldehyde-p-nitrophenylhydrazone (A) melted as follows :

A, %	0	24·8	36·2	50·0	61·2	76·0	100
M. p.	178°	157°	143°	145°	160°	174°	190°

Interconversion. (a) With 1·45N-sodium ethoxide at 85°. Either azomethine was treated with the catalyst for 1 hour, and, after isolation in the usual way and addition of 2N-sulphuric acid, was steam-distilled in a current of carbon dioxide, in an all-glass apparatus. Benzaldehyde present in the distillate was estimated as the p-nitrophenylhydrazone.

Isomeride.	Wt. taken.	Wt. of hydrazone.	(II), %.
I	0·100	0·130	12·8
II	0·100	0·136	13·4

The equilibrium ratio is therefore I(87) $\rightleftharpoons$ II(13), and these figures are used in calculating the velocity coefficients given below.

(b) With 0·145N-sodium ethoxide at 82°. Owing to difficulties attending m. p. determination with mixtures of hydrazones containing much p-dimethylaminobenzaldehyde-p-nitrophenylhydrazone, and to the small range of conversion of the isomeride I, attention was directed largely toward the equilibration of II.

Isomeride used.	Time with NaOEt, hrs.	Yield, %.	M. p.	Isomeride (II), %.	$k_1 + k_2$ (hrs.$^{-1}$).
I {	0	100·5	179°	0	—
	15	97	173	8	0·063
	72	96	167	15	—
II {	72	95	165	17	—
	54	97	163	19	0·050
	42	96	161·5	21	0·056
	15	98	154 *	53	0·052
	12	98	158	60	0·051
	0	100	190	100	—

Equilibrium : II (13) $\rightleftharpoons$ I (87); $k_1 + k_2$ (mean) = 0·054 hr.$^{-1}$; $k_1/k_2 =$ 0·149; $k_1 = 0·007$; $k_2 = 0·047$.

* A first addition of p-dimethylaminobenzaldehyde-p-nitrophenylhydrazone did not alter the m. p.; a second addition produced an elevation.

Methyl Compounds.—p-*Methylbenzylidenebenzylamine* (as I) is a water-clear liquid, b. p. 210°/25 mm., solidifying to a mass of rectangular prisms, m. p. 27° (Found : C, 85·5; H, 7·1. $C_{15}H_{15}N$ requires C, 86·1; H, 7·2%).

p-*Methylbenzylamine.* The base was obtained (a) by reduction of p-toluonitrile (Krober, *Ber.*, 1890, **23**, 1030), (b) by reduction of p-tolualdoxime with 3% sodium amalgam in the presence of acetic acid; it had b. p. 105°/22 mm., m. p. 20—21°, and gave a picrate, m. p. 204° (decomp.) (compare Krober, *loc. cit.*; Lustig, *Ber.*, 1895,

28, 2988), and an acetyl derivative, m. p. 111° (compare Lustig, *loc. cit.*).

Benzylidene-p-*methylbenzylamine* (as II). Despite several attempts the *azomethine* could not be obtained as a constant-boiling liquid; the b. p. varied from 190—196°/20 mm., and the liquid rapidly became yellow on keeping (Found : C, 85·5; H, 7·5. $C_{15}H_{15}N$ requires C, 86·1; H, 7·2%).

Mixtures of p-tolualdehyde- and benzaldehyde-p-nitrophenyl-hydrazone (A) melted as follows :

A, %......	0	16·0	32·0	48·0	55·2	58·0	63·1	71·8	77·7	100
M. p.	196·5°	189·5°	182°	174°	170·5°	167°	166°	173°	178°	190°

Interconversion. (*a*) With 1·45N-sodium ethoxide at 85°. Treatment of (I) for 2 hours afforded a mixture of hydrazones, m. p. 171°; the isomeride (II) by similar treatment gave a product, m. p. 163°, and longer treatment did not raise this figure. Since (I) is a crystalline solid, the equilibrium ratio II(55) $\rightleftharpoons$ I(45), corresponding with the m. p. 171°, is preferred.

(*b*) With 0·145N-sodium ethoxide at 82°. Owing to the doubtful purity of (II), the velocity measurements were made with the isomeride (I) only.

Isomeride used.	Time with NaOEt, hrs	Yield, %.	M. p.	Isomeride (II), %.	$k_1 + k_2$ (hrs.$^{-1}$).
	0	100	196·5°	0	—
	1	99	191	12·5	0·262
	2·1	99	184	27	0·323
	3	90	180·5	35	0·335
	4	93	177·5	41	0·340
I	5	92·5	176	44	0·320
	6	—	175	46	0·258
	7	—	172	52	0·414
	9	94	170·5	55	—
	12	94	171	55	—
	18	—	170·5	55	—
II	0	100	190	100	—

Equilibrium : II (55) $\rightleftharpoons$ I (45); $k_1 + k_2$ (mean) $= 0.322$ hr.$^{-1}$; $k_1/k_2 = 1.222$; $k_1 = 0.177$; $k_2 = 0.145$.

Trimethylammonium Compounds.—N-*Benzyl*-ω-*imino*-p-*tolyltri-methylammonium iodide* (as I). The salt is readily prepared by warming p-dimethylaminobenzylidenebenzylamine with methyl iodide (1 mol.), diluted with an equal volume of chloroform; after precipitation from acetone solution with ether, it separates from dry alcohol in yellow prisms, m. p. 159—160° (Found : C, 52·8; H, 5·7; ionic I, 34·6. $C_{17}H_{21}N_2I$ requires C, 53·7; H, 5·6; I, 33·4%). The *salt* readily loses methyl iodide, since by treatment with p-nitro-phenylhydrazine under the standard conditions a 97% yield of p - dimethylaminobenzaldehyde - p - nitrophenylhydrazone, m. p. (crude) 179°, m. p. (crystallised) 181·5°, mixed m. p. 181·5°, is

obtained.   Treatment with 0·145N-sodium ethoxide at 82° also causes fission, since the same hydrazone, m. p. 179°, is obtained after 5 mins.' heating, and only after some hours can traces of benzaldehyde-p-nitrophenylhydrazone be isolated; this indicates that the system is controlled by the dimethylamino-group, and not by the trimethylammonium pole.

N-*Benzylidene-ω-amino*-p-*tolyltrimethylammonium iodide* (as II). Similarly prepared from benzylidene-p-dimethylaminobenzylamine and methyl iodide (1 mol.), the *salt* separates from acetone–ether in pale yellow pearly plates, m. p. 181° (Found :   C, 53·0;   H, 5·6. $C_{17}H_{21}N_2I$ requires C, 53·7;   H, 5·6%), and with p-nitrophenyl-hydrazine gives a quantitative yield of benzaldehyde-p-nitrophenyl-hydrazone.

Nitro-compounds.—p-Nitrobenzylidenebenzylamine (as I), m. p. 56°, and benzylidene-p-nitrobenzylamine (as II), m. p. 71° (compare Ingold and Piggott, J., 1922, **121**, 2381), yielded hydrazones quantitatively by fission with p-nitrophenylhydrazine, but underwent decomposition by even the briefest treatment with 0·145N-sodium ethoxide at 82°.

The following were obtained in an attempt to determine the effect of the acetamido-group on mobility and equilibrium :

p-*Acetamidobenzylidenebenzylamine* (as I), m. p. 158° after crystallisation from xylene (Found :   C, 76·4;   H, 6·25. $C_{16}H_{16}ON_2$ requires C, 76·2;   H, 6·4%), although giving a quantitative yield of p-acetamidobenzaldehyde·p-nitrophenylhydrazone,   appeared   to undergo decomposition by treatment with 0·145N·sodium ethoxide at 82°, since only a 60% yield of hydrazones, decreased by prolonged washing with 10% acetic acid, could be obtained.   Attempts to prepare the isomeride (II) were unsuccessful; p·acetamidobenzyl-amine could not be obtained by reduction of p-acetamidobenzald-oxime, m. p. 211°, neither was reduction of p·acetamidobenzonitrile (m. p. 202°, obtained from the oxime with acetic anhydride in pyridine) more successful.   Condensation of p-aminobenzylamine [*monopicrate*, red laminæ from methyl alcohol, m. p. 163° (Found : C, 44·6;   H, 3·8. $C_{13}H_{13}O_7N_5$ requires C, 44·4;   H, 3·7%) ; *dipicrate*, yellow prisms from methyl alcohol, decomposing without melting above 250° (Found :   C, 39·3;   H, 2·9. $C_{19}H_{16}O_{14}N_8$ requires C, 39·3;   H, 2·8%)] with benzaldehyde (1 mol.), and subsequent acetylation also failed to yield (II).