CCCXXIII.—*Dynamic Isomerism involving Mobile Hydrocarbon Radicals. Part III. Some Effects of Substitution on the Velocity of Interchange and Position of Equilibrium of Isomeric Triarylbenzenylamidines.*

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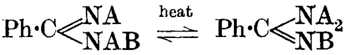
In Parts I and II of this series (J., 1929, 2133; preceding paper) the reversible rearrangement of the isomeric triarylamidines (I) and (II), where A and B are aryl groups, was described and shown

(I.)  (II.)

$$\mathrm{Ph{\cdot}C}{<}\begin{matrix}\mathrm{NA}\\ \mathrm{NAB}\end{matrix}\ \overset{\text{heat}}{\rightleftharpoons}\ \mathrm{Ph{\cdot}C}{<}\begin{matrix}\mathrm{NA_2}\\ \mathrm{NB}\end{matrix}$$

to resemble in certain respects the apparently irreversible change of imino-aryl ethers into amides.

$$\text{(III.)}\quad \mathrm{NAr'{:}CPh{\cdot}OAr} \xrightarrow{\text{heat}} \mathrm{NArAr'{\cdot}CPh{:}O}\quad \text{(IV.)}$$

It is known that the velocity of rearrangement of the imino-aryl ethers is greatly affected by substitution either in the migrating group (Ar) or in the group (Ar′) attached to the nitrogen atom (J., 1927, 1743), and it therefore seemed of interest to study the effects of substitution on the amidine change, especially as the position of equilibrium would be involved as well as the velocity of interconversion.

In a pair of isomerides such as (I) and (II), migration of a group A or B can only occur from the singly bound nitrogen atom to that originally carrying a double bond. When A leaves either $\cdot NA_2$ or $\cdot NAB$ it produces an isomeride, but when B leaves $\cdot NAB$ it attaches itself to $\colon NA$ and thus yields the original compound. Whilst there is no doubt that B does migrate from one nitrogen atom to the other, its transfer cannot be observed, and a pair of isomerides of this type may therefore be treated as consisting of (*a*) a migrating group A, and (*b*) a system $-NB\cdot CPh\cdot NA-$ in which the group A is migrating.

The enquiry is thus resolved into the determination of: (i) the effect of a given substitution, (*a*) in the migrating group or (*b*) in the group A or B of the system, on the velocity of interchange; (ii) the effect of similar substitution on the position of equilibrium; (iii) the effects on velocity and equilibrium of substitution in the phenyl group attached to the central carbon atom, a problem not dealt with in this communication.

Four pairs of isomerides have been investigated:

(*a*) $NPh\colon CPh\cdot NPh(C_7H_7)$ (Ia) $\rightleftharpoons$ $NPh_2\cdot CPh\colon N(C_7H_7)$ (IIa); $A = Ph$, $B = C_7H_7(p)$

(a repetition under improved conditions of the observations of Part I).

(*b*) $N(C_7H_7)\colon CPh\cdot NPh(C_7H_7)$ (Ib) $\rightleftharpoons$ $N(C_7H_7)_2\cdot CPh\colon NPh$ (IIb); $A = C_7H_7(p)$, $B = Ph$.

(*c*) $NPh\colon CPh\cdot NPh(C_6H_4Cl)$ (Ic) $\rightleftharpoons$ $NPh_2\cdot CPh\colon N(C_6H_4Cl)$ (IIc); $A = Ph$, $B = C_6H_4Cl\ (p)$.

(*d*) $N(C_6H_4Cl)\colon CPh\cdot NPh(C_6H_4Cl)$ (Id) $\rightleftharpoons$ $N(C_6H_4Cl)_2\cdot CPh\colon NPh$ (IId); $A = C_6H_4Cl\ (p)$, $B = Ph$.

The compounds were heated for various times at the standard temperature of 330—331° (corr.), and the extent of rearrangement was determined by the method described in Part I. Since prolonged exposure at the high temperature was always accompanied by a certain amount of decomposition, the heating was not continued long enough for equilibrium to be attained; the position of equilibrium was therefore calculated from the relative extent to which each member of a pair of isomerides had undergone rearrangement after the same exposure.

The results obtained may be summarised as follows :

Pair.	Group A.	Group B.	$(k + k') \times 10^3$.	Equilibrium % of (I), (NA:CPh·NAB).
(*a*)	Phenyl	*p*-Tolyl	6·2	69
(*b*)	*p*-Tolyl	Phenyl	2·0	53
(*c*)	Phenyl	*p*-Chlorophenyl	4·5	59
(*d*)	*p*-Chlorophenyl	Phenyl	11·3	71

Pairs (*a*) and (*b*) differ from one another only as regards the migrating group A. The relative rates of interconversion of the members of the two pairs represent, therefore, the relative mobilities of the groups phenyl and *p*-tolyl in the same system. A comparison of the velocities of transformation of pairs (*c*) and (*d*) similarly gives the relative values for phenyl and *p*-chlorophenyl. The mobilities of these three groups are therefore in the order *p*-tolyl<phenyl<*p*-chlorophenyl. This is also the order of their relative attraction for electrons as measured by the dissociation constants of the corresponding acids ($R{\cdot}CO_2H$), and the result to be expected from analogy with the imino-ether change.

The effect of substitution in the group B of the system on the mobility of a given migrating group A can be seen by comparison of pairs (*a*) and (*c*); phenyl is the mobile group in both pairs, but (*c*) possesses a *p*-chlorophenyl group in place of the *p*-tolyl group of (*a*). The effect of this substitution is to render the members of pair (*c*) less easily interconvertible than those of (*a*), which again might be expected, since replacement of one group (Ar′) attached to the nitrogen atom of an imino-aryl ether (III) by another having a greater electron affinity causes a diminution of the rate of change of the ether into the amide.

In view of the close resemblances between the amidine and imino-ether rearrangements in structural form, in their intramolecular character, and in the effects of substitution on the velocity of rearrangement, the conclusion cannot be resisted that the two isomeric changes are identical in their mode of occurrence.

If the distribution of groups in the molecules of an equilibrium mixture of the isomeric amidines (I) and (II) were determined solely by chance, the mixture would contain 2 parts of (I) to 1 part of (II), but since A and B are different groups they might affect the position of equilibrium by exerting some directing influence on the mobile group. In each case the equilibrium was found to be displaced from the ideal value of 67% of (I), and by consideration of the direction of this displacement it is now possible to decide between the view originally put forward (J., 1927, 1744) and that recently suggested (Bennett, *Ann. Reports*, 1929, **26**, 123) as to the way in which the rearrangement of the imino-ethers, and hence of the amidines, takes place.

According to the original view the retarding effect upon the rearrangement of an imino-aryl ether (III) of a group (Ar′) having a powerful attraction for electrons is due to a constraint upon the valency electrons of the migrating group (Ar) exerted by Ar′ through the chain. In the amidine system the influence of such a group would be exerted in one isomeride through the chain, as in the imino-ethers, and in the other, directly on the nitrogen atom to which the mobile group was attached. The latter influence would certainly be the more powerful, and hence the migrating group would tend to remain on that nitrogen atom which carried the group with the greater attraction for electrons.

According to the more recent suggestion, instead of the initial step of the imino-ether change being the severance of one of the binding electrons from the oxygen atom, it is considered more likely that the migrating group would first attract one or both of the lone electrons of the nitrogen atom and then release the original binding pair. The new hypothesis is also in complete agreement with all the observed effects of substitution on the velocity of the imino-ether rearrangement, but leads to a different prediction of the displacement of equilibrium in the amidine system. The retardation of isomeric change caused by the presence of an electron-attracting group in the system is regarded as due to a constraint imposed upon the electrons of that nitrogen atom to, and not from, which the migrating group is proceeding. The retardation will therefore be greater when the mobile group is attached to the end of the system away from the electron-attracting group X (VI to IX), and the compounds in which this condition is fulfilled (VI and VIII) will therefore tend to accumulate at the expense of their isomerides (VII and IX), thus :

$$\text{(VI.)}\quad \mathrm{NX{:}CPh{\cdot}NY_2} \rightleftarrows \mathrm{NXY{\cdot}CPh{:}NY} \quad \text{(VII.)}$$

$$\text{(VIII.)}\quad \mathrm{NX{:}CPh{\cdot}NXY} \rightleftarrows \mathrm{NX_2{\cdot}CPh{:}NY} \quad \text{(IX.)}$$

From the positions of equilibrium of the four pairs of isomerides investigated, it is evident that the mobile group tends, only slightly in pair (*a*), but quite definitely in the other three cases, to attach itself preferentially to the nitrogen atom which carries the group with the lesser attraction for electrons. The view originally put forward for the imino-ether rearrangement must therefore be modified according to the more recent suggestion.

The influence of substitution in the migrating group upon the position of equilibrium is small compared with that of substitution in the system. The relative values for the pairs of mono-*p*-chlorophenyl- and di-*p*-chlorodiphenyl-amidines indicate that the nature of the migrating group exerts no influence upon the equilibrium attained, whilst those for the mono-*p*-tolyl and di-*p*-tolyl pairs agree with this conclusion within the possible limits of experimental error.

EXPERIMENTAL.

The amidines were all prepared from the corresponding anilide-iminochlorides and secondary amines by the method described in Part I.

NN'-*Di*-p-*tolyl*-N-*phenylbenzenylamidine* (I*b*) crystallised from light petroleum in microscopic yellow crystals, m. p. 133° (Found : N, 7·4. $C_{27}H_{24}N_2$ requires N, 7·45%).

N-*Di*-p-*tolyl*-N'-*phenylbenzenylamidine* (II*b*) was obtained in long yellow needles from alcohol, m. p. 149·5—150° (Found : N, 7·45%).

NN'-*Diphenyl*-N-p-*chlorophenylbenzenylamidine* (I*c*) formed clusters of microscopic yellow needles, m. p. 150—152°, sparingly soluble in a mixture of equal parts of acetone and alcohol (Found : Cl, 9·05. $C_{25}H_{19}N_2Cl$ requires Cl, 9·3%).

N-*Diphenyl*-N'-p-*chlorophenylbenzenylamidine* (II*c*) crystallised from the same solvent in stout yellow needles, m. p. 167·5—168·5° (Found : Cl, 9·4%).

NN'-*Di*-p-*chlorodiphenyl*-N-*phenylbenzenylamidine* (I*d*) formed yellow crystals, m. p. 132—133°, fairly readily soluble in the same mixture of solvents (Found : Cl, 17·1. $C_{25}H_{18}N_2Cl_2$ requires Cl, 17·0%).

N-*Di*-p-*chlorodiphenyl*-N'-*phenylbenzenylamidine* (II*d*), clusters of fine yellow needles, m. p. 101—103°, was readily soluble in alcohol (Found : Cl, 16·8%).

The constitution of each of these amidines was confirmed by the isolation and identification of the primary and secondary amines formed on hydrolysis with concentrated hydrochloric acid in a sealed tube for 6 hours at 200—230°. Aniline and *p*-toluidine were obtained as their acetyl derivatives, and the identity of each compound was established by the method of mixed melting points.

Dynamical Experiments.—As minute traces of impurity were found to accelerate the charring of the amidines at the temperature of the experiments, some specimens were recrystallised several times after a constant melting point had been attained, until a direct test showed that very little darkening occurred on heating for 2 hours at 330—340°.

5 G. of amidine were used for each determination. The material, in a test-tube, was plunged into an oil-bath of about 5 gallons capacity, electrically heated and maintained between 330° and 331° (corr.) throughout the experiment. At the end of the required period, the tube was withdrawn and the contents were analysed by

the method described in Part I. Several tubes of each of a pair of isomeric amidines were heated together. The short time required for the material to attain the temperature of the bath was ignored. In view of the low volatility of di-*p*-chlorodiphenylamine, glycerol (50 c.c.) was added to the mixture (approx. 100 c.c.) for each steam distillation involving this substance, to raise the boiling point of the aqueous liquid. Control analyses of mixtures of isomeric amidines in known proportions showed that the results were accurate to within less than 5% and in most cases to within 2%.

*Melting points of mixtures of phenyl-*p*-tolylamine and di-*p*-tolylamine.*

$(C_7H_7)_2NH$ (% by wt.)	100	90	80	70	60	50
$(C_7H_7)_2NH$ (mols. %)	100	89·3	78·8	68·3	58·3	48·2
M. p.	80·5°	75·0°	69·7°	63·0°	57·8°	62·5°
$(C_7H_7)_2NH$ (% by wt.)	40	30	20	10	0	
$(C_7H_7)_2NH$ (mols. %)	38·2	28·3	18·8	9·35	0	
M. p.	69·2°	75·2°	81·0°	84·8°	89·0°	

*Melting points of mixtures of diphenylamine and *p*-chlorodiphenylamine.*

$(C_6H_4Cl)PhNH$ (% by wt.)	100	91·2	80·4	68·1	59·7	50·2
$(C_6H_4Cl)PhNH$ (mols. %) ...	100	89·6	77·3	64·0	55·3	45·7
M. p.	70·6°	65·3°	59·9°	52·5°	45·7°	38·8°
$(C_6H_4Cl)PhNH$ (% by wt.)	39·3	31·3	22·6	9·3	0	
$(C_6H_4Cl)PhNH$ (mols. %) ...	35·0	27·5	19·5	8·0	0	
M. p.	36·3°	40·5°	45·0°	50·5°	55·0°	

*Melting points of mixtures of *p*-chlorodiphenylamine and di-*p*-chlorodiphenylamine.*

$(C_6H_4Cl)PhNH$ (% by wt.)	100	89·8	79·9	69·9	60·0	50·2
$(C_6H_4Cl)PhNH$ (mols. %) ...	100	91·1	82·3	73·1	63·7	54·1
M. p.	70·6°	65·9°	61·0°	55·9°	50·0°	46·8°
$(C_6H_4Cl)PhNH$ (% by wt.)	40·1	30·0	19·7	10·0	0	
$(C_6H_4Cl)PhNH$ (mols. %) ...	44·1	33·4	22·3	11·5	0	
M. p.	54·3°	61·0°	67·0°	72·6°	78·4°	

The results of the various series of dynamical experiments are summarised in the following tables. Small errors in the analyses give rise to much larger variations in the values of the velocity coefficient. In order, therefore, to bring out more clearly the substantial concordance of the results, this coefficient has first been worked out for each observation, and then, from the mean of the figures thus obtained, together with the mean value deduced for the position of equilibrium, the values for the percentage change of each isomeride have been calculated. These are shown in the tables against the corresponding experimental data. Time is expressed in minutes and logarithms to the base 10 are used throughout.

Conversion of (I*a*) *and* (II*a*) *into equilibrium mixture at* 330—331°.

Mean value of $k + k' = 6{\cdot}2 \times 10^{-3}$. Equilibrium at 69% (I*a*).

Time.	% Change (I*a*) → (II*a*), found.	calc.	% Change (II*a*) → (I*a*), found.	calc.	Equilibrium % (I*a*).
20	7	8	17	17	70·5
40	12	13·5	28·5	30	70·5
60	19	18	41	39·5	69
90	25·5	22·5	48·5	50·5	66
120	28	25·5	55	56·5	67
					Mean 69

Conversion of (I*b*) *and* (II*b*) *into equilibrium mixture at* 330—331°.

Mean value of $k + k' = 2{\cdot}0 \times 10^{-3}$. Equilibrium at 53% (I*b*).

Time.	% Change (I*b*) → (II*b*), found.	calc.	% Change (II*b*) → (I*b*), found.	calc.	Equilibrium % (I*b*).
40	10	8	8	9	44
60	13·5	11·5	12	12·5	47
60	11	11·5	11	12·5	50
90	19	16	21	18	52
90	17	16	18	18	51
120	18·5	20	23	22·5	55·5
120	18	20	20·5	22·5	53·5
180	24	26·5	38	30	61·5
180	23	26·5	28·5	30	55·5
240	30	31·5	40	35·5	56·5
240	25	31·5	32	35·5	56·5
					Mean 53

Conversion of (I*c*) *and* (II*c*) *into equilibrium mixture at* 330—331°.

Mean value of $k + k' = 4{\cdot}5 \times 10^{-3}$. Equilibrium at 59% (I*c*).

Time.	% Change (I*c*) → (II*c*), found.	calc.	% Change (II*c*) → (I*c*), found.	calc.	Equilibrium % (I*c*).
20	8	8	13	11	61·5
40	13	14	20	20	61
60	19	19	26·5	27·5	58·5
90	25·5	25	36	35·5	58·5
120	30	29	38·5	42	56·5
					Mean 59

Conversion of (I*d*) *and* (II*d*) *into equilibrium mixture at* 330—331°.

Mean value of $k + k' = 11{\cdot}3 \times 10^{-3}$. Equilibrium at 71% (I*d*).

Time.	% Change (I*d*) → (II*d*), found.	calc.	% Change (II*d*) → (I*d*), found.	calc.	Equilibrium % (I*d*).
20	11·5	11·5	26·5	29	70
30	15·5	15·5	40	38·5	72
40	18·5	18·5	47·5	46	72
60	22	23	56	56	72
60	25	23	54·5	56	69
					Mean 71

We desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant to one of us (A. W. C.) that has defrayed part of the cost of this investigation.

THE UNIVERSITY, SHEFFIELD. [*Received, September* 16*th*, 1930.]