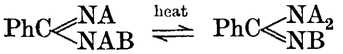
# 237. *Dynamic Isomerism involving Mobile Hydrocarbon Radicals. Part IV. The Rearrangement of 3 : 5-Dichloro-substituted Triphenylbenzenylamidines.*

By ARTHUR WILLIAM CHAPMAN and CHARLES HARDY PERROTT.

IN Part III (J., 1930, 2462) the interconversion of a number of pairs of isomeric triarylamidines (I and II, where A and B are different aryl groups) was described, and a detailed view of the course of the rearrangement put forward.

(I.)  (II.)

$$\mathrm{PhC}\!<\!\substack{\mathrm{NA}\\ \mathrm{NAB}} \overset{\text{heat}}{\rightleftharpoons} \mathrm{PhC}\!<\!\substack{\mathrm{NA_2}\\ \mathrm{NB}}$$

In order to study a further series of compounds of the same type in which the effects of substitution on the velocity of rearrangement and on the position of equilibrium might be expected to be greater, the *o*-chloro-substituted amidines (A = Ph, B = *o*-chlorophenyl, and conversely) were first prepared, but they were found to be unsuitable owing to the occurrence of an alternative reaction at temperatures below that of isomeric change (see following paper). The complete series of 3 : 5-dichloro-substituted compounds (Ie, IIe, If IIf) was therefore synthesised, and the interconversion of the isomeric pairs studied at the standard temperature of 330—331° (corr.).

$$\text{(e)}\ \mathrm{NPh{:}CPh{\cdot}NPh{\cdot}C_6H_3Cl_2}\ \text{(Ie)} \rightleftharpoons \mathrm{NPh_2{\cdot}CPh{:}N{\cdot}C_6H_3Cl_2}\ \text{(IIe)},$$
$$\mathrm{A = Ph,\ B = C_6H_3Cl_2}\ (3:5).$$

$$\text{(f)}\ \mathrm{N(C_6H_3Cl_2){:}CPh{\cdot}NPh{\cdot}C_6H_3Cl_2}\ \text{(If)} \rightleftharpoons \mathrm{N(C_6H_3Cl_2)_2{\cdot}CPh{:}NPh}\ \text{(IIf)}$$
$$\mathrm{A = C_6H_3Cl_2;\ B = Ph.}$$

The results obtained, together with those of the previous series, may be summarised as follows :

| Pair. | Group A. | Group B. | % I at equilibrium. | $(k+k')$ $\times 10^3$. | $k \times 10^3$. | $k' \times 10^3$. |
|---|---|---|---|---|---|---|
| a | Ph | $p$-$C_7H_7$ | 69 | 6·2 | 1·9 | 4·3 |
| b | $p$-$C_7H_7$ | Ph | 53 | 2·0 | 0·95 | 1·05 |
| c | Ph | $p$-$C_6H_4Cl$ | 59 | 4·5 | 1·85 | 2·65 |
| d | $p$-$C_6H_4Cl$ | Ph | 71 | 11·3 | 3·3 | 8·0 |
| e | Ph | 3 : 5-$C_6H_3Cl_2$ | 47 | 3·2 | 1·7 | 1·5 |
| f | 3 : 5-$C_6H_3Cl_2$ | Ph | 77 | 109·0 | 25·0 | 84·0 |

The effects of the introduction of the 3 : 5-dichlorophenyl group into the amidine molecule were in complete agreement with the requirements of the theory discussed in Part III (*loc. cit.*) and were considerably greater than those produced by the different substituents of pairs a to d. The data for pairs a, c, and e, which differ only with respect to group B, show that the influence of this group in the system on the ease of molecular rearrangement is exerted almost entirely on one of the two opposed isomeric changes. Whilst the velocity constants ($k'$) for the change II ⟶ I vary widely from pair to pair, those ($k$) for the reverse change I ⟶ II are practically constant. It is therefore only the migration of a group to :NB that is affected by a change of group B, a fact which lends additional support to the view that the first and controlling step in the rearrangement is the attraction of the lone electrons of the doubly bound nitrogen atom by the migrating group.

The conclusion that in any one system the nature of the migrating group has little effect on the position of equilibrium was confirmed. Despite their wide divergence in mobility, the phenyl and the 3 : 5-dichlorophenyl group exerted, as migrating groups, no influence on the position of equilibrium outside the limits of experimental error.

The reversible amidine rearrangement and the completed iminoether change are qualitatively closely similar both in the conditions

$$\mathrm{NB{:}CPh{\cdot}OA} \longrightarrow \mathrm{NAB{\cdot}CPh{:}O} \text{ (where A and B are aryl groups)}$$

under which they take place and in the effects of substitution on the velocity of rearrangement. One interesting quantitative difference is, however, apparent. When in either system a migrating group A is replaced by another having a greater attraction for electrons (as measured by the dissociation constant of the corresponding acid A·$CO_2H$), the velocity of rearrangement is increased. Similar substitution in group B causes a retardation of the isomeric change. The relative values of the velocity constants for a number of iminoethers are given in the following table and are calculated from the data already recorded (J., 1927, 1750). Being derived from only a few observations in each case, they are not of high accuracy, but they are sufficiently exact to show clearly that in the imino-ether series the ratio in which the velocity constant is decreased by a given substitution on the nitrogen atom (group B), whilst somewhat less than that by which the value is increased by similar substitution in group A, is of the same order.

Relative Values of the Velocity Constants of Rearrangement of Imino-ethers NB:CPh·OA ($k$ for NPh:CPh·OPh taken as unity).

Compounds NPh:CPh·OA (A varied, B = Ph).

| Group A. | $k$. |
|---|---|
| 2 : 4-Dichlorophenyl | 10·5 |
| *o*-Chlorophenyl | 4·6 |
| *m*-Chlorophenyl | 3·3 |
| *p*-Chlorophenyl | 1·9 |
| Phenyl | (1·0) |
| *p*-Anisyl | 0·8 |

Compounds NB:CPh·OPh (A = Ph, B varied).

| Group B. | $k$. | $1/k$. |
|---|---|---|
| 2 : 4-Dichlorophenyl | 0·32 | 3·1 |
| *o*-Chlorophenyl | 0·37 | 2·7 |
| *m*-Chlorophenyl | 0·50 | 2·0 |
| *p*-Chlorophenyl | 0·69 | 1·45 |
| Phenyl | (1·0) | (1·0) |
| *p*-Anisyl | 1·4 | 0·7 |

In the amidine series, however, the effect of substitution in group B (I and II) on the velocity of rearrangement is much less than that of similar substitution in the migrating group A, as shown in the next table, where *p*-chlorophenyl is used as the basis of comparison.

Substitution in the Migrating Group.

| Group A. | Relative values of $k+k'$.* |
|---|---|
| *p*-Tolyl | 0·13 |
| Phenyl | 0·4 |
| *p*-Chlorophenyl | 1·0 |
| 3 : 5-Dichlorophenyl | 13·6 |

Substitution in Group B of System (A = Ph).

| Group B. | Relative values of $k+k'$. | Relative values of $1/(k+k')$. |
|---|---|---|
| *p*-Tolyl | 1·4 | 0·7 |
| — | — | — |
| *p*-Chlorophenyl | 1·0 | 1·0 |
| 3 : 5-Dichlorophenyl | 0·7 | 1·4 |

* The values in this column are calculated from the relative mobilities compared with phenyl, the comparison in each case being made in the appropriate system NA·CPh·NPh (compare J., 1930, 2464).

The differences in the second list are only slightly increased if $k'$ is substituted for $k + k'$.

A possible explanation of this difference between the imino-ether and amidine systems is that the constraint exerted by the group B on the lone electrons of the attached nitrogen atom is partly compensated by an electromeric adjustment thus :

$$A_2N{-}CPh{=}\overset{\longrightarrow}{NB} \qquad AO{-}CPh{=}\overset{\longrightarrow}{NB}$$

Owing, however, to the greater tendency of nitrogen to pass into the " onium " condition as compared with oxygen the compensation is more complete and the relative effect of any given change in B is therefore less pronounced in the amidines than in the imino-ethers.

## EXPERIMENTAL.

The amidines were all prepared from the appropriate anilideiminochlorides and secondary amines by the method described in Part I (J., 1929, 2133). The secondary amines required were obtained from the corresponding primary amines and phenols through the iminoethers (J., 1929, 569).

*Benzo*-3 : 5-*dichloroanilide*, crystallised from alcohol, had m. p. 147° (Found : Cl, 26·6. $C_{13}H_9ONCl_2$ requires Cl, 26·7%); it yielded *benzo*-3 : 5-*dichloroanilideiminochloride*, m. p. 41°, b. p. 231—232°/16—20 mm., on treatment with phosphorus pentachloride (Found : Cl, 37·25. $C_{13}H_8NCl_3$ requires Cl, 37·4%).

N-3 : 5-*Dichlorophenylbenziminophenyl ether* crystallised from alcohol in thick plates, m. p. 69—70° (Found : Cl, 20·7. $C_{19}H_{13}ONCl_2$ requires Cl, 20·75%), and on heating at 300—310° for 2 hours yielded *benzoyl*-3 : 5-*dichlorodiphenylamine*, m. p. 107—109° (Found : Cl, 20·65%), from which 3 : 5-*dichlorodiphenylamine*, m. p. 41—42°, b. p. 222—224°/25 mm., was obtained by hydrolysis with alcoholic potash (Found : Cl, 29·7. $C_{12}H_9NCl_2$ requires Cl, 29·8%).

N-3 : 5-*Dichlorophenylbenzimino*-3 : 5-*dichlorophenyl ether*, crystallised from alcohol, had m. p. 71° (Found : Cl, 34·3. $C_{19}H_{11}ONCl_4$ requires Cl, 34·55%).

*Benzoyl*-3 : 5 : 3′ : 5′-*tetrachlorodiphenylamine* crystallised in leaves, m. p. 135—136° (Found : Cl, 34·6%), and yielded on alkaline hydrolysis 3 : 5 : 3′ : 5′-*tetrachlorodiphenylamine*, crystals from alcohol, m. p. 160—161° (Found : Cl, 46·1. $C_{12}H_7NCl_4$ requires Cl, 46·3%).

NN′-*Diphenyl*-N-3 : 5-*dichlorophenylbenzenylamidine* (Ie), crystallised from alcohol, had m. p. 112° (Found : Cl, 17·1. $C_{25}H_{18}N_2Cl_2$ requires Cl, 17·0%).

N-*Diphenyl*-N′-3 : 5-*dichlorophenylbenzenylamidine* (IIe) crystallised in long yellow needles, m. p. 94—95° (Found : Cl, 17·1%). NN′-*Di*-(3 : 5-*dichlorophenyl*)-N-*phenylbenzenylamidine* (If) formed an almost colourless, crystalline powder, m. p. 95—97° (Found : Cl, 29·35. $C_{25}H_{16}N_2Cl_4$ requires Cl, 29·25%).

N-*Di*-(3 : 5-*dichlorophenyl*)-N′-*phenylbenzenylamidine* (IIf) crystallised in tiny plates, m. p. 131—132° (Found : Cl, 29·2%). For compounds (If) and (IIf) the condensation of iminochloride and amine was completed by heating for 2 hours at 160—170°.

*Dynamical Experiments.*—The amidine (1·5 g.) was heated at 330—331° for given times as described in Part III (*loc. cit.*, p. 2466). The procedure previously adopted for the analysis of mixtures of isomeric amidines was found to be unsuitable in the present case and considerable difficulties were encountered in devising another method. We wish to express our grateful thanks to Professor G. M.

Bennett for much helpful advice on this matter whilst one of us was temporarily absent. The method finally adopted was as follows: The heated material was hydrolysed with concentrated hydrochloric acid for 6 hours at 200—230° in a sealed tube. The resulting mixture was made alkaline and distilled in steam until 150 c.c. of distillate had been collected which contained all the aniline and 3 : 5-dichloroaniline together with a little diphenylamine. To this were added 2*N*-sodium hydroxide (25 c.c.) and acetone (50 c.c.), all the amines then passing into solution, and the mixture was shaken with two successive portions of benzoyl chloride (each 1 c.c.). The benzoylated mixture was distilled in steam, the liquid being kept as nearly as possible constant in volume. The acetone was thus removed together with any secondary amine from the original distillate. The mixed benzoylamines were filtered off, and their melting point determined. Mixtures of aniline and 3 : 5-dichloroaniline in known proportions were benzoylated under identical conditions and from the melting-point curve thus obtained the composition of each amidine mixture was determined.

*M. p.'s of mixed benzoylamines obtained by benzoylation of mixtures of aniline and* 3 : 5-*dichloroaniline.*

| Mols.-% $C_6H_3Cl_2{\cdot}NH_2$ | 100 | 91·5 | 74 | 65·7 | 61·0 | 56·1 |
|---|---|---|---|---|---|---|
| M. p. .................... | 147·5° | 144·0° | 135·5° | 128·0° | 123·5° | 116·0° |
| Mols.-% $C_6H_3Cl_2{\cdot}NH_2$ | 55·6 | 49·8 | 43·2 | 31·6 | 24·6 | 0 |
| M. p. .................... | 119·0° | 124·5° | 132·0° | 142·5° | 147·0° | 160·0° |

The results of the dynamical experiments are in the following tables. Time is expressed in minutes, and logarithms to the base 10 are used throughout.

*Conversion of* (Ie) *and* (IIe) *into equilibrium mixture at* 330—331°.

Mean value of $k + k' = 3{\cdot}2 \times 10^{-3}$. Equilibrium at 47% (Ie).

| Time. | % Change (Ie) ⟶ (IIe), found. | calc. | % Change (IIe) ⟶ (Ie), found. | calc. | Equilibrium % (Ie). |
|---|---|---|---|---|---|
| 60 | 20 | 19 | 18·5 | 17 | 48 |
| 120 | 29 | 31 | 28 | 28 | 49 |
| 180 | 39 | 39 | 31 | 35 | 44·5 |
| 200 | 42·5 | 41 | 36·5 | 36 | 46 |

*Conversion of* (If) *and* (IIf) *into equilibrium mixture at* 330—331°.

Mean value of $k + k' = 109 \times 10^{-3}$. Equilibrium at 77% (If).

| Time. | % Change (If) ⟶ (IIf), found. | calc. | % Change (IIf) ⟶ (If), found. | calc. | Equilibrium % (If). |
|---|---|---|---|---|---|
| 2 | 11 | 9 | 29 | 30·5 | 72·5 |
| 3 | 12 | 12 | 40 | 41 | 77 |
| 5 | 15 | 16·5 | 55 | 55 | 79 |
| 6 | 19·5 | 18 | 59·5 | 60 | 75·5 |
| 10 | 20·5 | 21 | 71·5 | 71 | 79 |
| 15 | 21 | 22·5 | 77 | 75 | 79 |
| 30 | 24 | 23 | 77 | 77 | 77 |

*Conversion of* (If) *and* (IIf) *into equilibrium mixture at* 310—311°.

Mean value of $k + k' = 39{\cdot}4 \times 10^{-3}$. Equilibrium at 77% (If).

| Time. | % Change (If) → (IIf), found. | calc. | % Change (IIf) → (If), found. | calc. | Equilibrium % (If). |
|---|---|---|---|---|---|
| 10 | 16·5 | 13·5 | 42·5 | 46 | 72 |
| 25 | 21 | 20·5 | 69 | 69 | 76·5 |
| 40 | 22 | 22·5 | 77 | 75 | 78 |
| 60 | 23 | 23 | 77 | 76·5 | 77 |

We wish 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 research.

THE UNIVERSITY, SHEFFIELD. [*Received, April 5th*, 1932.]