CCLXXV.—*Dynamic Isomerism involving Mobile Hydrocarbon Radicals. Part I. The Triarylbenzenylamidines.*

By Arthur William Chapman.

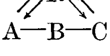
Isomeric changes involving the migration of a proton or anion or consisting merely of the redistribution of valency bonds in the molecules of the isomerides are frequently reversible. On the other hand, molecular rearrangements that involve the migration of a hydrocarbon radical nearly always take place in one direction only. Many of these completed isomeric changes (*e.g.*, the conversion of imino-ethers into amides, which corresponds with imidol-amido-prototropy) are structurally analogous to well-known cases of tautomerism, but the equilibrium between the two isomerides, if it exists, lies so far on one side that it cannot be detected.

During an investigation of the imino-aryl ethers (J., 1925, **127**, 1992; 1926, 2296; 1927, 1743) it was found that, whilst *N*-phenylbenziminophenyl ether (I) underwent isomeric change into benzoyldiphenylamine (II) to the extent of at least 99·9% (the limit of the analytical method), the rearrangement of the corresponding thioether (III) was probably reversible.

(I.) $OPh\cdot CPh{:}NPh$ $O{:}CPh\cdot NPh_2$ (II.) $SPh\cdot CPh{:}NPh$ (III.)

The belief in the reversibility of the change was based upon the identity and nature of the products of thermal decomposition of the imino-thioether and thioamide, but could not be regarded as satisfactorily established. The conditions necessary for rearrangement were so drastic as to cause decomposition of both isomerides and to render impossible either the isolation of the imino-thioether from the thioamide or the detection of an equilibrium between the two compounds.

It was therefore decided to examine some other triad system in which the expected equilibrium might be more readily observed.

In selecting the compounds for study, the following considerations were taken into account: (1) The two ends (A, C) of the triad  $\overset{R}{A\text{—}B\text{—}C}$ should be very nearly alike in order that the two isomerides may exhibit the least possible difference in stability. (2) The compounds must not decompose easily when heated, for a high temperature may be required to effect rearrangement. (3) The isomerides should be obtained by some method which leaves no doubt as to their constitution. Their structures must also be demonstrated independently by some analytical process.

Preliminary experiments indicated that the two diphenyl-*p*-tolylbenzenylamidines (IV and V) would be suitable for investigation.

$$\text{(IV.)}\quad Ph_2N{\cdot}CPh{:}N{\cdot}C_7H_7 \qquad\qquad PhN{:}CPh{\cdot}NPh{\cdot}C_7H_7\quad \text{(V.)}$$

Both ends of the triad were nitrogen atoms, the phenyl and *p*-tolyl groups were very similar, and the amidine system $NR'{:}CPh{\cdot}NHR$ was well known to be prototropic. Compounds (IV) and (V) decompose and darken only very slowly at 350°. They were prepared by condensation of an anilideiminochloride with the appropriate secondary amine, *e.g.*,

$$Ph_2NH + Cl{\cdot}CPh{:}N{\cdot}C_7H_7 \longrightarrow Ph_2N{\cdot}CPh{:}N{\cdot}C_7H_7 + HCl,$$

a process that clearly demonstrated their structure. Hydrolysis with concentrated hydrochloric acid at 200—220° yielded the corresponding primary amine, secondary amine, and benzoic acid, *e.g.*,

$$Ph_2N{\cdot}CPh{:}N{\cdot}C_7H_7 \xrightarrow{+H_2O} NHPh_2 + Ph{\cdot}CO_2H + NH_2{\cdot}C_7H_7$$

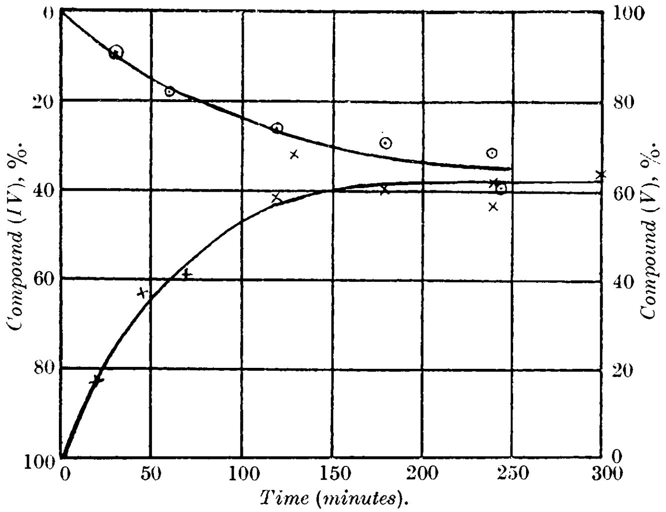
When compound (IV) was heated for an hour at 280—300° little change took place, but when the temperature was raised to 300—320° a new material, m. p. about 140°, was recovered on crystallisation of the melt from alcohol. After (IV) had been heated at 330—340° for two hours no unchanged substance could be recovered, but large quantities of the new material were obtained. This had the same composition and molecular weight as the original compound, but on hydrolysis it yielded a mixture of diphenylamine, phenyl-*p*-tolylamine, primary amines, and benzoic acid, and therefore appeared to be a mixture of both isomerides. All attempts to separate the mixture were unavailing, but when an artificial mixture of (IV) and (V) in the ratio 1 : 2 was crystallised from alcohol an entirely similar material separated from the solution.

It was therefore evident that, at the high temperature employed, partial conversion of one isomeride into the other had occurred.

Samples of (IV) and of (V) were then heated at 322—323° for various times, and the ratio of the two isomerides in each melt was estimated to within about 5% by the method described in the experimental section. The results obtained are shown in the figure. It will be seen that the two compounds underwent interconversion by migration of a phenyl group, yielding finally an equilibrium mixture containing 60—65% of (V).

It must be concluded, therefore, that the phenomenon of dynamic isomerism, well known in the cases of mobile hydrogen, anions, or valency bonds, extends also to mobile hydrocarbon radicals. Whilst, however, there is complete structural similarity between the tautomerism of amidines of the type NR′:CR·NR″H and the present case, the migration of the aryl group requires much more drastic conditions than does the migration of the proton. Dynamic isomerism involving mobile organic radicals is probably entirely different in mechanism from the other " tautomeric " changes. The latter have generally been shown to be intermolecular. depending upon the catalytic activity of the reagents employed to bring about the change, whilst the phenomenon now described, as judged from its close analogy with the transformation of imino-aryl ethers into amides, is intramolecular in character.

FIG. 1.



It is interesting to note that the amounts of compounds (IV) and (V) contained in the equilibrium mixture are approximately in the ratio 1 : 2, which would be expected if the distribution of the aryl groups on the nitrogen atoms were governed solely by chance. This is not surprising when the close similarity between the phenyl and *p*-tolyl groups is recalled. When, however, the effects of substitution on the rearrangement of the imino-ethers are borne in mind (J., 1927, 1743), it is probable that the replacement by other radicals of one or more groups in the amidines now studied will exert a marked influence both upon the mobility of the migrating group and upon the position of equilibrium attained. Experiments to determine the nature and magnitude of this influence are now in progress.

EXPERIMENTAL.

Preparation of the Isomeric Amidines.—Benz-*p*-toluidideiminochloride (or benzanilideiminochloride) (about 15 g.) was fused and weighed into a large test-tube. An equivalent amount of diphenylamine (or phenyl-*p*-tolylamine) was added, the mixture well stirred, and the tube heated in a bath of boiling water for 2 hours. The glassy mass was broken out of the tube, powdered, warmed with an excess of pyridine (50 c.c.) to remove the hydrogen chloride, and poured into water. The amidine separated as an oil which set rapidly to a hard crystalline mass and was then crystallised from alcohol.

N-*Diphenyl*-N′-p-*tolylbenzenylamidine* (IV) crystallised in microscopic pale yellow needles, m. p. 170—171° (Found : N, 7·7. $C_{26}H_{22}N_2$ requires N, 7·7%), sparingly soluble even in hot alcohol. After it had been heated with concentrated hydrochloric acid in a sealed tube at 200—220° for 6 hours, *p*-toluidine (identified as its acetyl derivative, m. p. 147—148°), diphenylamine (m. p. 52—54°), and benzoic acid (m. p. 122°), were obtained. The identities of these substances and of those obtained by hydrolysis of (V) were confirmed by the method of mixed melting points.

NN′-*Diphenyl*-N-p-*tolylbenzenylamidine* (V) (Found : N, 7·7%), microscopic yellow crystals sparingly soluble in alcohol, appeared to be dimorphous : if heated slowly it melted at 173—174°, but when plunged into a bath at 140° it melted at once, and then after being cooled and again heated it melted at 173—174°. There was no loss of weight when the compound was heated in a steam-oven for a few hours, but the product melted at 173—174° and did not do so if plunged into a bath at 140°. Aniline (identified as acetanilide, m. p. 110—113°), phenyl-*p*-tolylamine (m. p. 88—90°), and benzoic acid (m. p. 122—123°) were obtained on hydrolysis.

The phenyl-*p*-tolylamine required for the preparation of (V) was obtained from benzanilideiminochloride and *p*-cresol by the method recently described (this vol., p. 569). An over-all yield of 67% of recrystallised phenyl-*p*-tolylamine was obtained calculated on the iminochloride used. The intermediate compounds were used directly without purification.*

---

* In the preparation of imino-aryl ethers from anilideiminochlorides and sodium phenoxides in alcoholic solution, it is usually only necessary to have an excess of about 10 mols. % of phenol over the sodium. A large excess of resorcinol was employed in the first preparation of this kind (J., 1922, **121**, 1679) in order to avoid the formation of any appreciable amount of its disodium compound.

Preliminary Experiments on Compound (IV).—After this compound (5 g.) had been heated in an oil-bath at 280—300° for 50 minutes, only a slight depression of the freezing point (to 165°) was noted, and the heating was therefore continued at 310—330° for a further 40 minutes. On crystallisation of the cooled material from alcohol, slightly impure unchanged substance was recovered (3·1 g., m. p. 163—165°, raised to 166—167° by recrystallisation from dibutyl ether), and then 0·7 g. of material, m. p. 137—141° (Found: N, 7·75; *M*, by Rast micro-method, 316. Calc. for $C_{26}H_{22}N_2$: N, 7·7%; *M*, 362), which still melted at 138—140° after recrystallisation from dibutyl ether, but gave mixed m. p.'s of 152—160° with (IV) and 160—164° with (V).

Quantities of 20 and 100 g. of (IV) were then heated at 330—340° for 2 hours. No unchanged substance was recovered from these melts, but only material similar to that obtained in the first experiment (m. p. *ca.* 140°, indefinite). Numerous attempts to obtain pure substances by crystallisation from or extraction with various solvents, or by conversion into a picrate were all unsuccessful.

3 G. of this material were hydrolysed with concentrated hydrochloric acid at 200—220°. The mixture was made alkaline and distilled in steam. The first 70 c.c. contained most of the primary amines. These were dissolved in hydrochloric acid and filtered from the small quantity of oily secondary amines. On neutralisation, followed by acetylation with acetic anhydride, a crude acetyl compound was obtained (0·45 g.; m. p. 108—115°), which melted after recrystallisation from water at 130—136° (impure aceto-*p*-toluidide). A further 700 c.c. of distillate was collected and contained an oil which solidified on keeping (1·05 g., m. p. 65—70°), and after recrystallisation from light petroleum melted at 80—81° (mixed m. p. with phenyl-*p*-tolylamine, 82—84°). This could not have been produced by hydrolysis of the original amidine (IV). The solution remaining in the distillation flask deposited benzoic acid (0·7 g., m. p. 121—122°) when acidified.

5 G. of (IV) and 10 g. of (V) were cautiously fused together, and on crystallisation from alcohol (200 c.c.) the mixture was similar to that obtained by heating (IV) [11·3 g.; m. p. 138—140°, 140—141° after recrystallisation from alcohol, 139—143° when mixed with material from heating of (IV)].

Quantitative Experiments on the Interconversion of the Isomeric Amidines.—A number of test-tubes, each containing 5 g. of (IV) or (V), were immersed in a well-stirred oil-bath at 322—323°. At stated intervals a tube was withdrawn from the bath, and when quite cold the material was broken out of the tube and roughly powdered. About 3 g. were then hydrolysed with concentrated hydrochloric acid (25 c.c.) in a sealed tube at 200—220° for 6 hours. The hydrolysed mixture was made alkaline with concentrated potassium hydroxide and distilled in steam. To the distillate (1 litre) was added one-ninth of its volume of concentrated hydrochloric acid, the mixture was shaken, cooled, and kept for 1—2 hours. The insoluble secondary amines were filtered off, washed with water, and dried in the air. They were mixed by being fused together, and cooled rapidly, and the m. p. of the mixture was determined. The relative proportions of the two amines present were then ascertained from the melting-point curve which had previously been constructed for mixtures of the pure substances, and the composition was confirmed by a mixed m. p. determination with the nearest artificial mixture of the two amines. Preliminary experiments with mixtures of the two amidines in known proportions showed that the results thus obtained were accurate to within about 5%.

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

$NHPh{\cdot}C_7H_7$ (% by wt.)	0	9·6	21·3	29·7	37·8	48·6	59·7	68·7	81·3	91·0	100
$NHPh{\cdot}C_7H_7$ (mols. %)	0	8·9	19·9	28·0	36·0	46·6	57·7	67·0	80·0	90·3	100
M. p.	55·9°	50·7°	45·1°	43·5°	52·0°	60·6°	69·5°	74·2°	80·7°	85·0°	88·5°

Conversion of (IV) *into equilibrium mixture.*

Time (mins.)	20	45	70	120	129	180	240	240	300
M. p. of mixture of amines	46·1°	52·7°	56°	69·8°	75°	71°	72°	68·8°	73·2°
(V), %	17	37	41	58·5	68	60·5	62	57	64

Both this and the following table each include the results of two separate series of experiments.

Conversion of (V) *into equilibrium mixture.*

Time (mins.)	30	60	120	180	240	245
M. p. of mixture of amines	85°	82°	78·1°	76·5°	75·7°	70·9°
(V), %	90	82	74	71	69	61

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant that has defrayed part of the cost of this investigation.

THE UNIVERSITY, SHEFFIELD. [*Received, July 19th, 1929.*]