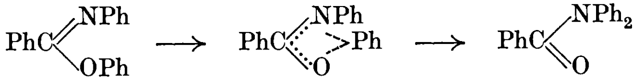
# CCXXVII.—*Imino-aryl Ethers. Part V. The Effect of Substitution on the Velocity of Molecular Rearrangement.*

By Arthur William Chapman.

In Part III (J., 1925, **127**, 1992), it was shown that *N*-phenylbenziminophenyl ether (I) could be completely converted into benzoyldiphenylamine (II) on heating. The change, which is unimolecular, was found to be best represented in terms of partial valencies (compare Robinson, *Mem. Manc. Lit. Phil. Soc.*, 1920, **64**, No. 4; Mumm, Hesse, and Volquartz, *Ber.*, 1915, **48**, 379) thus :

(I.)



(II.)

When translated into the terms of the electronic theory, this formulation is ambiguous, since the migrating group may (*a*) carry with it both its shared electrons, (*b*) leave them behind, or (*c*) carry one and leave the other.

It seemed desirable to study the effect of replacing the migrating phenyl group in *N*-phenylbenziminophenyl ether by other groups, since according to (*a*) it would be expected that the relative attraction for electrons and the velocity of migration of different groups would follow the same order, but according to (*b*) the two values should be in the opposite order, whilst if (*c*) were correct the velocity of migration of a group should be independent of its attraction for electrons.

A number of *N*-phenylbenzimino-ethers, RO·CPh:NPh (III), having different groups (R) attached to the oxygen atom, were made and their velocities of rearrangement were compared. A special experiment showed that these changes were not appreciably reversible. It was found that the groups could be arranged in the following order of descending ease of migration : *o*-nitrophenyl > 2 : 4 : 6-trichlorophenyl > *p*-acetylphenyl > 2 : 4-dichlorophenyl > *o*-chlorophenyl > *m*-chlorophenyl > *p*-chlorophenyl and α- and β-naphthyls > phenyl and *o*-anisyl > *m*-anisyl > *p*-anisyl > methyl.

The velocities of migration of these groups are in the same order as the dissociation constants of the corresponding carboxylic acids and phenols (R·CO$_2$H and R·OH) and it must therefore be concluded that the mechanism of the isomeric change is represented by (*a*). Steric effects were evidently negligible, since the *o*-substituted compounds underwent rearrangement more rapidly than the corresponding *m*- and *p*-compounds.

Confirmatory evidence was then sought from the effect, on the velocity of migration of a standard (phenyl) group, of variation of the groups attached to the nitrogen and carbon atoms. A number of *N*-substituted benziminophenyl ethers (IV) and *N*-phenylaryliminophenyl ethers (V) were accordingly prepared.

$$\text{(IV.)}\ \mathrm{PhO{\cdot}CPh{:}NR} \qquad\qquad \mathrm{PhO{\cdot}CR{:}NPh}\ \text{(V.)}$$

The greater the attraction of the group R for electrons in either (IV) or (V), the less readily will the oxygen atom release the electrons which bind it to the phenyl group, and hence, according to mechanism (*a*), the lower will be the velocity of rearrangement of the imino-ether.

This was indeed found to be the case, the ease of migration of the phenyl group being in the following order: *for various groups attached to the nitrogen atom* (*type* IV) *p*-anisyl > phenyl > *p*-chlorophenyl and α-naphthyl > *m*- and *o*-chlorophenyl and 2 : 4-dichlorophenyl > 2 : 4 : 6-trichlorophenyl, *and for various groups attached to the carbon atom* (*type* V) *p*-anisyl > phenyl > *p*- and *o*-chlorophenyl > *p*-nitrophenyl and 2 : 4 : 6-trichlorophenyl.

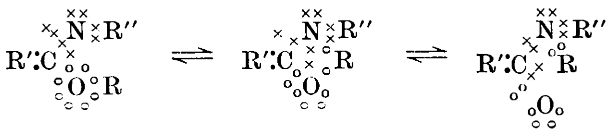
The isomeric change to a substituted amide which occurs when an imino-ether is heated at a sufficiently high temperature,

$$\mathrm{RO(or\ RS){\cdot}CR'{:}NR''} \rightleftharpoons \mathrm{O(or\ S){:}CR'{\cdot}NRR''},$$

has now been studied in some detail (compare Part III, *loc. cit.*; Part IV, J., 1926, 2296). The rearrangement has been shown to be intramolecular and does not require any detectable amount of a catalyst. The behaviour of the imino-thioethers showed that, as might be expected, the change is reversible, but in the oxygen ethers equilibrium occurs so far over to the amide side that the reversibility is not appreciable.

The velocity of isomeric change varies greatly with the nature of the migrating group and of the groups attached to the carbon and nitrogen atoms. The greater the attraction of the migrating group for electrons (*i.e.*, the more " negative " it is) the greater the velocity of change, whilst negative groups attached to the carbon and nitrogen atoms retard the rearrangement.

These facts are readily explicable on the assumption that the migrating group carries over to the nitrogen atom the two covalency electrons by which it is bound to the oxygen atom, and the isomeric change can be expressed in symbolic form thus :



(where × represents an electron originally belonging to the nitrogen octet, and o one belonging to the oxygen octet).

The iminoether–amide rearrangement is a typical triad change, and it seems highly probable that the mechanism of a number of other such changes will be found to be explicable in similar terms.

## EXPERIMENTAL.

The new imino-ethers required were prepared from the corresponding anilideiminochlorides and phenols by the method used for preparing *N*-phenylbenzimino-*m*-hydroxyphenyl ether (J., 1922, **121**, 1679). Unless otherwise stated, they were crystallised from alcohol, in which they were readily soluble when hot, but only sparingly soluble in the cold.

They were converted into the corresponding amides by heating at 280—310°, the products being purified by crystallisation from alcohol. Where possible, the amides thus obtained were compared directly with specimens prepared by other methods. The identity of two samples of a compound obtained from different sources was always confirmed by the method of mixed melting points.

N-*Phenylbenzimino*-m-*chlorophenyl ether* crystallised in colourless needles, m. p. 71° (Found : N, 4·6. $C_{19}H_{14}ONCl$ requires N, 4·55%). On heating, it was converted into benzoyl-*m*-chlorodiphenylamine (m. p. 101—102°; identical with an authentic specimen).

N-*Phenylbenzimino*-2 : 4-*dichlorophenyl ether*, pale yellow, slender prisms, m. p. 73—74° (Found: N, 4·2. $C_{19}H_{13}ONCl_2$ requires N, 4·1%).

N-*Phenylbenzimino*-2 : 4 : 6-*trichlorophenyl ether*, colourless plates, m. p. 80—81° (Found : N, 3·95. $C_{19}H_{12}ONCl_3$ requires N, 3·7%).

N-*Phenylbenzimino*-o-*anisyl ether*, colourless, slender prisms, m. p. 113° (Found : N, 4·7. $C_{20}H_{17}O_2N$ requires N, 4·6%).

N-*Phenylbenzimino*-m-*anisyl ether* was obtained as a viscous oil which did not crystallise even after standing for 18 months (Found : N, 4·45%). The product of heating this imino-ether was also not obtained in crystalline form.

N-*Phenylbenzimino*-p-*anisyl ether*, colourless plates, m. p. 79—80° (Found : N, 4·8%).

N-*Phenylbenzimino*-p-*nitrophenyl ether*, pale yellow plates, m. p. 76—77° (Found: N, 8·9. $C_{19}H_{14}O_3N_2$ requires N, 8·8%). All attempts to cause this imino-ether to undergo isomeric change were unsuccessful. Decomposition with formation of tar occurred even at 150°.

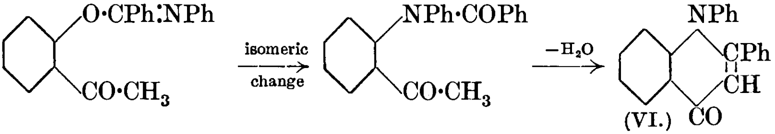
N-*Phenylbenzimino*-α-*naphthyl ether* crystallised from light petroleum in crusts, m. p. 89° (Found: N, 4·6. $C_{23}H_{17}ON$ requires

N, 4·3%). On heating, it gave benzoylphenyl-α-naphthylamine (m. p. 152°; identical with an authentic specimen).

N-*Phenylbenzimino*-β-*naphthyl ether* crystallised in thin leaflets from alcohol, in which it was only sparingly soluble at the boiling point; m. p. 127—128° (Found : N, 4·5%). It was hydrolysed by 50% sulphuric acid to β-naphthyl benzoate (m. p. 106—106·5°) and on heating gave benzoylphenyl-β-naphthylamine (m. p. 147°; identical with an authentic specimen).

N-*Phenylbenzimino*-p-*acetylphenyl ether*, m. p. 94—95° (Found : N, 4·6. $C_{21}H_{17}O_2N$ requires N, 4·45%).

N-*Phenylbenzimino*-o-*acetylphenyl ether*, m. p. 92—93° (Found : N, 4·6%). Instead of yielding benzoyl-*o*-acetyldiphenylamine when heated, it was converted into a basic compound, which crystallised from alcohol in thin leaves, m. p. 268°. The change was practically complete in 90 minutes at 267° (Found : C, 85·1; H, 5·1; N, 4·8; *M*, by Rast's micro-method, 285. $C_{21}H_{17}O_2N$ requires C, 80·0; H, 5·4; N, 4·45%; *M*, 315. $C_{21}H_{15}ON$ requires C, 84·8; H, 5·1; N, 4·7%; *M*, 297). The loss of a molecule of water had evidently occurred and 1 : 2-*diphenyl*-4-*quinolone* (VI) was formed thus,



(VI.)

the second stage being analogous to the formation of 4-hydroxy-2-phenylquinoline from benzoyl-*o*-aminoacetophenone (Camps, *Arch. Pharm.*, 1901, **239**, 597).

N-o-*Chlorophenylbenziminophenyl ether*, prepared from *benz*-o-*chloroanilideiminochloride* (b. p. 204°/10 mm.) and phenol, crystallised in slender prisms, m. p. 65—66° (Found : N, 4·4. $C_{19}H_{14}ONCl$ requires N, 4·55%). On heating, it was converted into benzoyl-*o*-chlorodiphenylamine (m. p. 95°; identical with an authentic specimen).

N-m-*Chlorophenylbenziminophenyl ether*, prepared from *benz*-m-*chloroanilideiminochloride* (b p. 211—213°/14 mm.), crystallised in rosettes of pale yellow, stout prisms, m. p. 66° (Found : N, 4·5%). It gave benzoyl-*m*-chlorodiphenylamine on heating (m. p. 100—101°; identical with an authentic specimen).

N-p-*Chlorophenylbenziminophenyl ether*, prepared from *benz*-p-*chloroanilideiminochloride* (b. p. 220—224°/20 mm.), formed stout prisms, m. p. 110° (Found : N, 4·4%). It yielded benzoyl-*p*-chlorodiphenylamine on heating (m. p. 110°; identical with an authentic specimen).

N-2 : 4-*Dichlorophenylbenziminophenyl ether*, stout prisms, m. p. 57—58° (Found : N, 4·0. $C_{19}H_{13}ONCl_2$ requires N, 4·1%). In this and several subsequent preparations the iminochloride was not distilled, but, after treatment of the anilide with phosphorus pentachloride and removal of the phosphorus oxychloride under reduced pressure on the water-bath, the residue was dissolved in dry ether and added directly to an alcoholic solution of sodium phenoxide.

N-2 : 4 : 6-*Trichlorophenylbenziminophenyl ether*, stout prisms, m. p. 88·5° (Found : N, 3·8. $C_{19}H_{12}ONCl_3$ requires N, 3·7%).

N-2 : 4 : 6-*Trichlorophenylbenzimino*-2 : 4 : 6-*trichlorophenyl ether*, colourless needles, m. p. 141°, sparingly soluble in boiling alcohol (Found : N, 3·0. $C_{19}H_9ONCl_6$ requires N, 2·9%). Heated at 250—260° for 2 hours, it was mostly recovered unchanged, but at 280—300° *benzoyl*-2 : 4 : 6 : 2′ : 4′ : 6′-*hexachlorodiphenylamine* (m. p. 194—195°. Found : N, 3·0%) was produced. The isomerisation of this imino-ether was therefore much slower than that of the corresponding *N*-phenylbenzimino-2 : 4 : 6-trichlorophenyl ether.

N-p-*Anisylbenziminophenyl ether*, prepared from *benz*-p-*anisidideiminochloride* (yellow flakes, m. p. 55°, b. p. 269—273°/162—180 mm. with some decomposition), formed yellow crystals, m. p. 100° (Found : N, 4·6. $C_{20}H_{17}O_2N$ requires N, 4·6%).

N-o-*Nitrophenylbenziminophenyl ether*, stout prisms, m. p. 67—68° (Found : N, 9·0. $C_{19}H_{14}O_3N_2$ requires N, 8·8%). Several unsuccessful attempts to cause rearrangement of this imino-ether were made. At 200—220°, it remained unchanged and above that temperature decomposed, giving much tar.

N-α-*Naphthylbenziminophenyl ether* formed a very viscous oil which would not crystallise (Found : N, 4·1. $C_{23}H_{17}ON$ requires N, 4·3%). On heating, it underwent isomeric change into benzoylphenyl-α-naphthylamine (m. p. 148—150°; identical with an authentic specimen).

N-*Methylbenziminophenyl ether* was prepared by Hantzsch's method (*Ber.*, 1893, **26**, 926) from benzmethylamideiminochloride and solid sodium phenoxide. It was obtained as colourless crystals, m. p. 30—31° (Found : N, 6·5. $C_{14}H_{13}ON$ requires N, 6·6%). On hydrolysis with 50% sulphuric acid, phenyl benzoate (m. p. 69—70°; not depressing the m. p. of an authentic specimen) was obtained. This imino-ether also decomposed without undergoing isomeric change.

N-*Phenyl*-o-*chlorobenziminophenyl ether*, prepared from o-*chlorobenzanilideiminochloride* (yellow prisms, m. p. 59°, b. p. 235°/60 mm.), formed colourless plates, m. p. 100° (Found : N, 4·8. $C_{19}H_{14}ONCl$ requires N, 4·55%).

N-*Phenyl*-p-*chlorobenziminophenyl ether*, from p-*chlorobenzanilide*-

*iminochloride* (b. p. 219°/17 mm.), formed pale yellow crusts, m. p. 64—65° (Found : N, 4·3%).

N-*Phenyl*-2 : 4 : 6-*trichlorobenziminophenyl ether*, colourless prisms, m. p. 94—95° (Found : N, 3·5. $C_{19}H_{12}ONCl_3$ requires N, 3·7%).

N-*Phenyl*-p-*methoxybenziminophenyl ether*, m. p. 86—87° (Found : N, 4·4. $C_{20}H_{17}O_2N$ requires N, 4·6%). This compound appeared to be dimorphous. On crystallisation from alcohol, long needles first appeared. These gradually dissolved and were replaced by stout prisms. No difference in the m. p.'s of the two forms was observed.

N-*Phenyl*-o-*nitrobenziminophenyl ether*, thin leaves, m. p. 141—142° (Found : N, 9·0. $C_{19}H_{14}O_3N_2$ requires N, 8·8%). Heated for 2 hours at 230—240°, the material remained practically unchanged. Above this temperature it decomposed, yielding a coke-like residue.

N-*Phenyl*-p-*nitrobenziminophenyl ether*, long, yellow prisms, m. p. 102—102·5° (Found : N, 8·55%).

*Benzoyl*-2 : 4-*dichlorodiphenylamine*, obtained by heating either *N*-phenylbenzimino-2 : 4-dichlorophenyl ether or *N*-2 : 4-dichlorophenylbenziminophenyl ether, formed crusts, m. p. 109° (Found : N, 4·2. $C_{19}H_{13}ONCl_2$ requires N, 4·1%).

*Benzoyl*-2 : 4 : 6-*trichlorodiphenylamine* was prepared from *N*-phenylbenzimino-2 : 4 : 6-trichlorophenyl ether and *N*-2 : 4 : 6-trichlorophenylbenziminophenyl ether and obtained in long prisms, m. p. 149° (Found : N, 3·75. $C_{19}H_{12}ONCl_3$ requires N, 3·7%).

*Benzoyl*-o-*methoxydiphenylamine*, prepared from *N*-phenylbenzimino-*o*-anisyl ether, formed hard crusts, m. p. 117° (Found : N, 4·7. $C_{20}H_{17}O_2N$ requires N, 4·6%).

*Benzoyl*-p-*methoxydiphenylamine*, obtained from either *N*-phenylbenzimino-*p*-anisyl ether or *N*-*p*-anisylbenziminophenyl ether, formed slender prisms, m. p. 121° (Found : N, 4·8%).

Contrary to the statement of Mumm, Hesse, and Volquartz (*loc. cit.*), *N*-phenylbenzimino-*o*-nitrophenyl ether underwent isomeric change at 165°. The dark oil obtained by heating this imino-ether (10 g.) for 1 hour at 165° was covered with ether; *benzoyl*-o-*nitrodiphenylamine* (4 g.) slowly crystallised in yellowish leaves, m. p. 134° (unchanged by recrystallisation from alcohol) (Found : N, 8·8. $C_{19}H_{14}O_3N_2$ requires N, 8·8%).

*Benzoyl*-p-*acetyldiphenylamine*, prepared from *N*-phenylbenzimino-*p*-acetylphenyl ether, formed leaves, m. p. 136—137·5° (Found : N, 4·4. $C_{21}H_{17}O_2N$ requires N, 4·45%).

Each of the following five amides was prepared by heating the corresponding imino-ether, and also from diphenylamine and the appropriate acid chloride.

o-*Chlorobenzoyldiphenylamine*, large prisms, m. p. 142—143° (Found : N, 4·8. $C_{19}H_{14}ONCl$ requires N, 4·55%).

p-*Chlorobenzoyldiphenylamine*, fine leaves, m. p. 138—138·5° (Found : N, 4·3%).

2 : 4 : 6-*Trichlorobenzoyldiphenylamine*, flat prisms, m. p. 118—119° (Found : N, 3·6. $C_{19}H_{12}ONCl_3$ requires N, 3·7%).

p-*Methoxybenzoyldiphenylamine*, prisms, m. p. 139—140° (Found : N, 4·3. $C_{20}H_{17}O_2N$ requires N, 4·6%).

p-*Nitrobenzoyldiphenylamine*, yellow prisms, m. p. 156—157° (Found : N, 9·05. $C_{19}H_{14}O_3N_2$ requires N, 8·8%).

2 : 4 : 6-*Trichlorobenzanilide*, prepared from 2 : 4 : 6-trichlorobenzoyl chloride and aniline, formed long needles, m. p. 197° (Found : N, 4·4. $C_{13}H_8ONCl_3$ requires N, 4·7%).

*Comparison of the Rates of Change of the Imino-ethers.*—The comparison was made by measuring the amount of change which took place when each compound was heated for a given time at a definite temperature. Test-tubes, each containing 2 g. of an imino-ether, were immersed together for the standard time (90 minutes) in a thermostat, strictly comparable results thus being obtained even if slight fluctuations occurred in the temperature.

As many of the mixtures thus obtained exhibited great reluctance to crystallise from the fused material, analysis by melting- or freezing-point methods was excluded, and therefore the following chemical method was adopted.

About 0·5 g. of the mixture was weighed into a stoppered flask and dissolved in dry ether, 25 c.c. of an approximately *N*/5-solution of sulphuric acid in dry ether were added, and the mixture was kept for 3 hours to permit complete separation of the imino-ether sulphate as crystals or as an oil. The liquid was then filtered into a separating funnel containing water, the residue and the filter were washed with a little dry ether, and the contents of the funnel were shaken and titrated with *N*/5-sodium hydroxide and phenolphthalein. The difference between this titration and a blank, in which 25 c.c. of the standard acid were used, corresponded with the amount of imino-ether in the weighed material. The estimation was carried out in duplicate.

Control experiments showed that this process gave results agreeing to within a few units % with the calculated figure, the imino-ether sulphate being assumed to have the formula $RO{\cdot}CR{:}NR,H_2SO_4$. The error appeared to be constant for each imino-ether and the results in the tables below have been corrected accordingly—the corrections do not affect the arrangement of the imino-ethers in order of ease of isomeric change.

The imino-ethers containing the 2 : 4 : 6-trichlorophenyl group and *N*-phenylbenzimino-*o*-nitrophenyl ether did not give insoluble sulphates by this method, and the products obtained from them were examined separately. In the case of *N*-phenylbenzimino-2 : 4 : 6-trichlorophenyl ether, the melting points of the heated samples were compared with those of known mixtures of the imino-ether and benzoyl-2 : 4 : 6-trichlorodiphenylamine. The products from the *N*- and *C*-trichlorophenyl compounds were crystallised from alcohol, and the unchanged compounds weighed. *N*-Phenylbenzimino-*o*-nitrophenyl ether underwent rearrangement at so low a temperature as to leave no doubt as to its position in the series.

The change of *N*-phenylbenziminomethyl ether was studied separately by Lander's method (J., 1903, **83**, 406) : 10 g., heated in a sealed tube at 300—330° for 2 hours, gave 2·5 g. of benzoylmethylaniline (m. p. after recrystallisation 57° ; did not depress the m. p. of an authentic specimen).

The results obtained were as follows :

O-*Substituted ethers*, RO·CPh:NPh.

| | Percentage changed in 90 mins. at | | | | | | |
|---|---|---|---|---|---|---|---|
| Group (R) on O atom. | 162—163°. | 200—201°. | 219—220°. | 242—243°. | 255°. | 266—267°. | 300—330°. |
| *o*-Nitrophenyl | >40 | | | | | | |
| 2 : 4 : 6-Trichlorophenyl | 0 | 87 | >91 | | | | |
| *p*-Acetylphenyl | | 39 | 76 | 92 | | | |
| 2 : 4-Dichlorophenyl | | 28 | 60 | 93 | | | |
| *o*-Chlorophenyl | | 16 | 27 | 77 | 91 | | |
| *m*-Chlorophenyl | | | | 63 | 84 | | |
| *p*-Chlorophenyl | | | | 46 | 62 | | |
| α-Naphthyl | | | | | 62 | 80 | |
| β-Naphthyl | | | | | 61 | 82 | |
| Phenyl | | | | 25 | 45 | 71 | |
| *o*-Anisyl | | | | | 47 | 74 | |
| *m*-Anisyl | | | | | 43 | 55 | |
| *p*-Anisyl | | | | | 25 | 44 | |
| Methyl | | | | | | | 25 |

N-*Substituted ethers*, PhO·CPh:NR.

| Group (R) on N atom. | % Change in 90 mins. at 267°. | 270°. | Group (R) on N atom. | % Change in 90 mins. at 267°. | 270°. |
|---|---|---|---|---|---|
| 2 : 4 : 6-Trichlorophenyl | <17 | — | *p*-Chlorophenyl | 56 | 61 |
| 2 : 4-Dichlorophenyl | 31 | 36 | α-Naphthyl | 61 | 63 |
| *o*-Chlorophenyl | 37 | 39 | Phenyl | 69 | 75 |
| *m*-Chlorophenyl | 47 | 49 | *p*-Anisyl | 80 | 85 |

C-*Substituted ethers*, PhO·CR:NPh.

| Group (R) on C atom. | % Change in 90 mins. at 267°. | 270°. | Group (R) on C atom. | % Change in 90 mins. at 267°. | 270°. |
|---|---|---|---|---|---|
| *p*-Nitrophenyl | 49 | 49 | *p*-Chlorophenyl | 61 | 62 |
| 2 : 4 : 6-Trichlorophenyl | <50 | <55 | Phenyl | 69 | 75 |
| *o*-Chlorophenyl | 63 | 63 | *p*-Anisyl | 85 | 84 |

Benzoyl-2 : 4 : 6-trichlorodiphenylamine and benzoyl-*p*-methoxydiphenylamine were unchanged after heating for 1 hour at 240—250°

and 250—270°, respectively, showing that the isomeric changes into these compounds were not appreciably reversible.

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