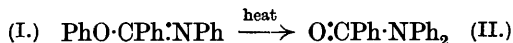


CCCIII.—*Imino-aryl Ethers. Part IV. Reversible Migration of an Aryl Group.*

By ARTHUR WILLIAM CHAPMAN.

IN Part III of this series (J., 1925, 127, 1992) it was shown that *N*-phenylbenziminophenyl ether (I) may be converted into benzoyl-diphenylamine (II) on heating, and that this change was unimolecular, complete and without by-products :

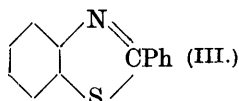


As the behaviour of the corresponding imino-thioether seemed likely to throw additional light on this isomeric change, *N*-phenylbenziminophenyl thioether (VI) and *N*-*p*-tolylbenziminophenyl thioether were prepared.

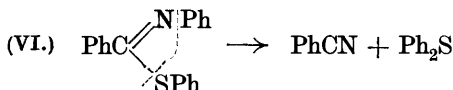
When *N*-phenylbenziminophenyl thioether (VI) was heated for 2 hours at 280—290°, a treatment which is sufficient to cause complete isomeric change of the *O*-ether, only a small amount of thio-

benzoyldiphenylamine (VII) was produced, most of the material being unchanged. The migration of the phenyl group from sulphur to nitrogen was therefore much more sluggish than that from oxygen to nitrogen in an otherwise similar case. Thiobenzoyldiphenylamine under similar conditions suffered practically no change.

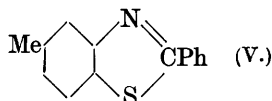
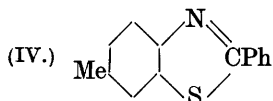
At higher temperatures, especially at 320° and above, decomposition of the imino-thioether took place, the products isolated being diphenyl sulphide, benzonitrile, thiophenol, and 1-phenylbenzthiazole (III).



The production of thiophenol and 1-phenylbenzthiazole is not easily explicable, but the diphenyl sulphide and benzonitrile, isolated in yields of up to 29%, can be regarded as derived by the disruption of the imino-thioether molecule, thus :

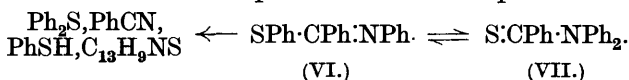


When *N-p*-tolylbenziminophenyl thioether was heated under similar conditions, 1-phenyl-5-methylbenzthiazole (IV) was produced and not 1-phenyl-4-methylbenzthiazole (V), so that the formation of the thiazole from the imino-thioether is effected, either by elimination of the group attached to the sulphur atom, or by previous migration of this group to the nitrogen atom.



The yields of 1-phenylbenzthiazole obtained by heating *N*-phenylbenziminophenyl thioether and thiobenzoyldiphenylamine, respectively, under identical conditions, were, however, not sufficiently different to enable a decision between these two views to be reached.

Thiobenzoyldiphenylamine, at 320° and above, yielded the same decomposition products as the imino-thioether in closely similar yields. It is not easy to see how diphenyl sulphide and benzonitrile and also thiophenol could be formed directly from a substance of the structure of thiobenzoyldiphenylamine, but the explanation at once becomes simple if it is assumed that *N*-phenylbenziminophenyl thioether is an intermediate product in the decomposition :



The conclusion therefore seems inevitable, that, although the high temperature at which the isomeric change takes place renders the attainment of an actual equilibrium impossible, the reaction here investigated is reversible, the phenyl group migrating between sulphur and nitrogen in either direction.

EXPERIMENTAL.

N-Phenylbenziminophenyl thioether was prepared from benzanilide-iminochloride and thiophenol by the method used for preparing *N*-phenylbenziminio-*m*-hydroxyphenyl ether (J., 1922, 121, 1679), all operations involving alkaline solutions of thiophenol being conducted in an atmosphere of nitrogen. It crystallised from alcohol in stout yellow prisms, m. p. 58° (Found: N, 4.98. $C_{19}H_{15}NS$ requires N, 4.84%), and was hydrolysed by 50% sulphuric acid to aniline and phenyl thiolbenzoate (m. p. 56—57°, not depressing the m. p. of an authentic specimen).

N-p-Tolylbenziminio-p-tolyl thioether, prepared similarly from benz-*p*-toluidideiminochloride and *p*-thiocresol, crystallised from alcohol in yellow prisms, m. p. 50° (Found: N, 4.64. $C_{21}H_{19}NS$ requires N, 4.42%). On hydrolysis by 50% sulphuric acid, it furnished *p*-toluidine (m. p. 43—44°) and *p*-tolyl thiolbenzoate (m. p. 76°), both identified by direct comparison with authentic specimens.

Incidentally, *thiobenzoyldi-p-tolylamine* was prepared by heating a finely powdered mixture of benzoyldi-*p*-tolylamine with half its weight of phosphorus pentasulphide in a boiling brine-bath. After treatment with sodium hydroxide to remove unchanged phosphorus pentasulphide and repeated crystallisation from alcohol, in which it was very sparingly soluble, it yielded orange crystals, m. p. 189—190° (Found: N, 4.64. $C_{21}H_{19}NS$ requires N, 4.42%).

Comparative Heating of N-Phenylbenziminophenyl Thioether and Thiobenzoyldiphenylamine.—5 G. of material were used for each experiment. After the heating, the product was extracted with ether (30—40 c.c.) and any insoluble matter filtered off. This always consisted of unchanged thiobenzoyldiphenylamine. The ethereal extract was saturated with hydrogen chloride and the insoluble hydrochlorides separated. The solution was washed with sodium hydroxide to remove acid and thiophenol, dried and evaporated, and any residue of thiobenzoyldiphenylamine was crystallised from alcohol. The precipitated hydrochlorides were warmed with concentrated hydrochloric acid to convert the iminothioether into phenyl thiolbenzoate and dissolve the 1-phenylbenzthiazole, which was then recovered by pouring the acid solution into water. Both products were crystallised from alcohol.

The 1-phenylbenzthiazole (m. p. 114°) was identified by analysis

(Found: N, 6.66. $C_{13}H_9NS$ requires N, 6.63%) and by direct comparison with an authentic specimen.

N-p-tolylbenzimidino-*p*-tolyl thioether, heated at 320° for 6 hours, yielded 1-phenyl-5-methylbenzthiazole (needles, m. p. 120—121°, not depressing the m. p. of a specimen prepared by the oxidation of thiobenz-*p*-toluidide, compare *Ber.*, 1886, **19**, 1068). Only small yields were obtained, and it was found that the substance readily chars under these conditions, whilst 1-phenylbenzthiazole is quite stable.

Identification of the Decomposition Products of N-Phenylbenzimidino-phenyl Thioether and of Thiobenzoyldiphenylamine.—The substance under examination (20 g.), contained in a Claisen flask, was gradually heated in a very slow current of carbon dioxide, the volatile decomposition products being collected in a freezing mixture. Distillation commenced at about 330—340° and this temperature was maintained until distillation ceased (1—2 hours). The distillate was a yellowish liquid with an odour of thiophenol and contained some crystals of 1-phenylbenzthiazole. Redistillation gave two main fractions, b. p.'s 160—210° and 280—310°, respectively. No material of b. p. lower than 160° was isolated. The lower-boiling fraction consisted of thiophenol and benzonitrile. The thiophenol was identified by its odour, solubility in sodium hydroxide, and conversion by benzoyl chloride into phenyl thiolbenzoate (m. p. 57—58°, not depressing the m. p. of an authentic specimen). The benzonitrile was identified, after separation from the thiophenol, by the formation of a brown, crystalline compound with hydriodic acid, and by conversion with potassium hydroxide into ammonia and benzoic acid (m. p. 119—121°, not depressing the m. p. of an authentic specimen). The fraction boiling at 280—310° consisted of diphenyl sulphide, identified by oxidation with potassium permanganate to diphenylsulphone (m. p. 124—125°, not depressing the m. p. of an authentic specimen), and with concentrated nitric acid to diphenylsulphone and its di- and tetra-nitro-derivatives (m. p.'s 194—195° and 240°, respectively).

The residue in the decomposition flask was repeatedly extracted with boiling concentrated hydrochloric acid, and the 1-phenylbenzthiazole recovered by pouring the extracts into water. A small amount of dark-coloured tarry matter remained undissolved in the acid.

The yields of decomposition products were the same from both the imino-thioether and the thiobenzoyldiphenylamine. In a number of experiments, 10—13% of the calculated amount of thiophenol was isolated as phenyl thiolbenzoate, 16—29% as diphenyl sulphide, and 35—40% as 1-phenylbenzthiazole.

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