

CXC.—10-*Chloro-5 : 10-dihydrophenarsazine and its Derivatives. Part X. The 1- and/or 3-Methyl Derivatives. The Condensation of Arsenious Chloride and Phenyl-m-tolylamine.*

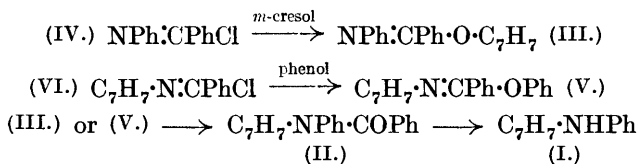
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At the time of the commencement of this series of investigations the study of the condensation of arsenious chloride and phenyl-*m*-tolylamine had to be postponed on account of the difficulty of access of the latter compound in a state of purity. Recently, however, Rasuwajew (*Ber.*, 1929, **62**, 1215), in connexion with the study of what are described as meriquinonoid compounds, recorded

the preparation of 10-chloro-1(or 3)-methyl-5 : 10-dihydrophenarsazine * by the above method, using the conditions set forth by Burton and Gibson (J., 1926, 460). The melting point of the product was given as 195—196°. Since both 1-methyl- and 3-methyl-10-chloro-5 : 10-dihydrophenarsazine have been rationally synthesised by the present authors (this vol., p. 767) and shown to be indistinguishable isomerides or one and the same substance, m. p. 215—216.5°, it seemed of importance to investigate whether the compound obtained by Rasuwajew was isomeric with the synthesised substance or substances.

The preparation of phenyl-*m*-tolylamine (I) of unquestionable purity has been accomplished by the methods described by Chapman (J., 1927, 1743; this vol., p. 569), to whom we wish to express our thanks for many useful practical suggestions.

N-Phenylbenziminom-*m*-tolyl ether (III) was prepared by condensing *N*-phenylbenziminochloride (IV) and *m*-cresol. On heating at 280—300°, this ether was converted into the isomeric benzoyl derivative of phenyl-*m*-tolylamine (II). The isomeric ether,



N-*m*-tolylbenziminophenyl ether (V), prepared in a similar manner from phenol and *N*-*m*-tolylbenziminochloride, gave the same benzoyl derivative on isomerisation. The phenyl-*m*-tolylamine was easily obtained from its benzoyl derivative by alkaline hydrolysis.

When arsenious chloride was condensed with phenyl-*m*-tolylamine under the conditions previously described (*loc. cit.*), a crystalline product, m. p. 195—201°, was obtained and after one crystallisation from benzene this gave small yellow needles which, alone or mixed with the rationally synthesised 1-methyl and 3-methyl-10-chloro-5 : 10-dihydrophenarsazines, melted at 215—216°, the identity thus being shown.

The low melting point of Rasuwajew's product may be due to the use of impure phenyl-*m*-tolylamine, the methods hitherto described for the preparation of this substance generally allowing of the possibility of its contamination with other secondary arylamines.

* It is somewhat confusing that two systems of nomenclature for this series of compounds are now in use. The compound obtained by Rasuwajew is described by him as "10-chloro-2(4)-methyl-9 : 10-dihydrophenarsazine."

EXPERIMENTAL.

N-Phenylbenziminochloride (IV) (Wallach, *Annalen*, 1876, **184**, 79; Gerhardt, *ibid.*, 1858, **108**, 217) has b. p. 173°/15 mm. *N*-*m*-Tolylbenziminochloride (VI) (Just, *Ber.*, 1886, **19**, 983) has b. p. 172°/8 mm. (yield, 57%).

N-*m*-Tolylbenziminophenyl Ether (V).—To phenol (9.4 g.) in a cooled solution of sodium ethoxide (alcohol, 40 c.c.; sodium, 2.3 g.) under a reflux condenser, a solution of *N*-*m*-tolylbenziminochloride (22.9 g.) in dry ether (50 c.c.) was slowly added with shaking. Heat developed and sodium chloride separated. After 16 hours, the ether and most of the alcohol were evaporated on the water-bath, water was added to the residue, the precipitated oil extracted with ether, the extract washed with dilute sodium hydroxide solution (some phenol being removed) and with water and dried with calcium chloride, and the ether evaporated. The residue, after standing under reduced pressure for some days, partly crystallised. This was triturated with alcohol, and the oily matter removed. The solid was recrystallised from a small quantity of alcohol, *N*-*m*-tolylbenziminophenyl ether separating in small colourless prisms (8 g.), m. p. 60° (Found: N, 4.9. $C_{20}H_{17}ON$ requires N, 4.9%).

N-Phenylbenzimino-*m*-tolyl ether (III) was prepared in a similar manner from *N*-phenylbenziminochloride (102 g.) in ether (220 c.c.), *m*-cresol (51 g.), alcohol (190 c.c.), and sodium (10.9 g.). It solidified after 5 days and when crystallised twice from a small quantity of alcohol formed colourless needles (48 g.), m. p. 65° (Found: N, 4.9%).

Benzoyl Derivative of Phenyl-m-tolylamine (Benzophenyl-m-tolylamide) (II).—(a) *N*-Phenylbenzimino-*m*-tolyl ether was heated at 280—300° for 2 hours. The benzoyl derivative, which solidified on cooling, crystallised from alcohol in colourless prisms (yield, 85%), m. p. 104—106° (Found: N, 4.9. $C_{20}H_{17}ON$ requires N, 4.9%).

(b) The recrystallised product obtained from *N*-*m*-tolylbenziminophenyl ether in a similar manner had m. p. 104—106° and was identical with that prepared by method (a).

Phenyl-*m*-tolylamine (15 g.) was obtained by hydrolysing the benzoyl derivative (35 g.) by Chapman's method (this vol., p. 571). After hydrolysis the greater part of the alcohol was evaporated, and the residue treated with water; the base was extracted in ether and finally distilled under reduced pressure. It had b. p. 183—184°/17 mm., and m. p. 27.5° (thermometer in substance).

Condensation of Arsenious Chloride and Phenyl-m-tolylamine.—A mixture of arsenious chloride (13.3 g.), phenyl-*m*-tolylamine (12.2 g.),

and *o*-dichlorobenzene (27 c.c.) was boiled for 5 hours. Hydrogen chloride was evolved and, on cooling, yellow crystalline material separated, filling the liquid. After being washed with *o*-dichlorobenzene and with benzene and recrystallised from benzene, it formed small yellow needles, m. p. 215—216° (Found : Cl, 12.4. Calc. : Cl, 12.2%).

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