

CXCI.—*Pyrolysis of Diazoamino-p-toluene.*

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THE first researches on the pyrolysis of diazoamines were made by Heusler (*Annalen*, 1890, **260**, 227), who heated these compounds either in sand or in liquid paraffin. Similar experiments on the heating of diazoaminobenzene in aniline were subsequently made by Hirsch (*Ber.*, 1892, **25**, 1973), who recommended this process as a means of obtaining *o*- and *p*-aminodiphenyls (*o*- and *p*-xenylamines: D.R.-P. 62309; Friedländer's "Fortschritte," **3**, 36; compare Aeschlimann, Lees, McClelland, and Nicklin, *J.*, 1925, **127**, 66). Recent improvements in the technology of diphenyl and its derivatives have, however, afforded more direct means of preparing these two bases (Jenkins, McCullough, and Booth, *Ind. Eng. Chem.*, 1930, **22**, 31; Morgan and Walls, *J. Soc. Chem. Ind.*, 1930, **49**, 15r).

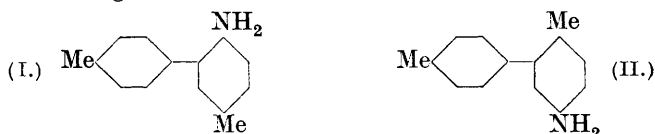
The foregoing researches showed that on pyrolysis diazoaminobenzene decomposed violently at 150°, evolving nitrogen and yielding *p*-aminoazobenzene, diphenylamine, *o*- and *p*-xenylamines, and small quantities of aniline, benzene, and diphenyl. To this list of pyrogenic products we would now add azobenzene, found in a repetition of Hirsch's experiment. In a comparative study of the pyrolysis of diazoamino-*p*-toluene and diazoamino-*p*-chlorobenzene Heusler found that both evolved nitrogen on heating, but he isolated only toluene and chlorobenzene respectively from the non-gaseous products of these decompositions, although the molecular configuration of the former diazoamine suggests that its pyrolysis should result in the production of a certain amount of *o*-aminoditolyl (I).

Pyrolysis of diazoamino-*p*-toluene in *p*-toluidine was attended by evolution of nitrogen at 150°, but in other respects the thermal changes differed considerably from those observed with diazoaminobenzene. Aminoazo-*p*-toluene and di-*p*-tolylamine were isolated only in small proportions and the total yield of aminoditolyls was

about 15% of the amount calculated. Quantitative estimations of the more volatile products of pyrolysis showed that toluene was the chief non-gaseous constituent and that nitrogen was always accompanied by ammonia.

Colouring matters such as indulines which arise in the pyrolysis of diazoaminobenzene were absent in this case. Azo-*p*-toluene was found in appreciable amount and, as this compound and toluene are both reduction products of diazoamino-*p*-toluene, the hydrogen required for their production must be sought in the resinification of a considerable proportion of the melt. The pitch left after extraction of the crystallisable products by petroleum consisted largely of acid-soluble resinamines similar to those obtained from low-temperature tar (*J. Soc. Chem. Ind.*, 1928, 47, 132T). The *p*-toluidine employed as solvent in the pyrolysis was recovered unchanged.

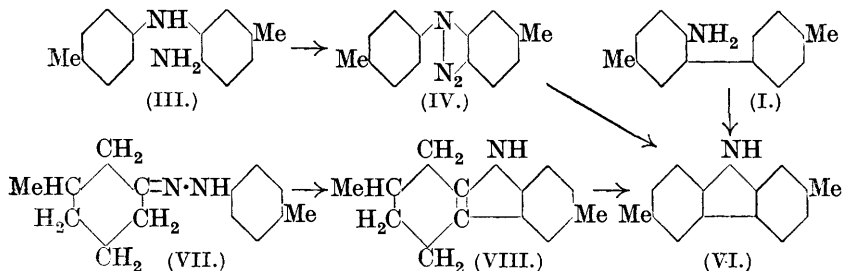
Isomeric Aminoditolyls.—The pyrolytic removal of nitrogen from diazoamino-*p*-toluene may be considered to yield two radicals, *p*-tolyl and *p*-iminotolyl, the union of which would result in the formation of di-*p*-tolylamine and of an aminoditolyl (I) in which the *p*-tolyl group enters the other ring in the ortho-position with respect to nitrogen.



The absence of any free para-position explains the small yield of aminoditolyl (compare Jacobsen, *Annalen*, 1922, 427, 148). The main basic product, which has been shown to have this constitution, is always accompanied by a small proportion of an isomeric amine which was first detected by its characteristic hydrochloride. Although the amount available of this by-product is too small for orientation experiments, it may be formulated provisionally as arising from the directive influence of the methyl group acting in opposition to that of the imino-residue (II). The constitution assigned to the main product, 2-amino-4':5-dimethyldiphenyl (4':5-dimethyl-2-xenylamine), was established by its pyrogenic conversion into 2:6-dimethylcarbazole (VI), a substance which would be a useful constitutional guide were it not for the confusion attaching to it in the literature.

2:6-Dimethylcarbazole.—Richter's "Lexicon" records 2:6-dimethylcarbazole, m. p. 208—209° (Borsche, Witte, and Bothe, *Annalen*, 1907, 359, 77), and 3:7-dimethylcarbazole, m. p. 224° (Ullmann, *Ber.*, 1898, 31, 1497). The alternative notation suggests

a structural identity, but as the disparity in melting points required elucidation, we have repeated the two preparations. Ullmann transformed hydrazo-*p*-toluene into the isomeric *o*-semidine (III), the triazole (IV) of which yielded 2 : 6-dimethylcarbazole (VI) on heating.



The *p*-tolylhydrazone (VII) of 3-methylcyclohexanone studied by Borsche, Witte, and Bothe loses ammonia to acid and becomes converted into a tetrahydrodimethylcarbazole (VIII). The constitution of this compound is not, however, defined completely by its mode of formation, since ring closure might have involved the carbon in position 2 of 3-methylcyclohexanone instead of carbon atom 6. Alternatively both condensations might have occurred concurrently with the formation of a mixture of two isomeric tetrahydrocarbazoles. However, oxidation of the product led solely to 2 : 6-dimethylcarbazole, m. p. 224°, identical with the two other preparations.

EXPERIMENTAL.

The diazoamino-*p*-toluene employed in the following experiments had been recrystallised from petroleum (b. p. 60—80°) and was in the form of yellow needles, m. p. 118°.

A preliminary heating of 10 g. of this diazoamine, which had been dried in a vacuum, with 25 g. of dry *p*-toluidine showed a slight evolution of nitrogen and ammonia at 120°, but with further rise of temperature the rate of gaseous evolution increased until at 150° the reaction became violent and exothermic, the temperature still rising without external application of heat. By operating under 5 mm. pressure, most of the *p*-toluidine present distilled away; the later fractions had a yellow tint due to azo-*p*-toluene, whereas the first runnings, when shaken with excess of 2*N*-hydrochloric acid to dissolve the base, left a light yellow, neutral oil which boiled at 110°, giving a colourless distillate identified as toluene.

I. *Quantitative Estimation of the more Volatile Products of Pyrolysis.*—(a) *Ammonia and toluene.* Quantities of diazoamino-*p*-toluene ranging from 5 to 8 g. were heated with three parts of

p-toluidine in a 50 c.c. distilling flask connected in series with a 10 c.c. graduated cylinder and a flask containing a measured quantity of *N*-hydrochloric acid. After the exothermic reaction had subsided, the temperature of the melt was raised until *p*-toluidine distilled. Heating was then stopped and air blown through the liquid to drive off all ammonia and toluene. The former was estimated alkalimetrically; the latter was measured directly in the graduated cylinder after the *p*-toluidine had been dissolved in 2*N*-hydrochloric acid. Calculated on a g.-mol. weight of diazoamino-*p*-toluene, the proportion of ammonia ranged from 0.31 to 0.35 g., whereas the amount of toluene varied from 40.2 to 44.1 g.

(b) *Nitrogen, ammonia and toluene.* The foregoing experimental details were modified so that the side tube of the graduated cylinder was connected with a Schiff nitrometer. One g. of the diazoamine in 4 g. of *p*-toluidine was pyrolysed in a stream of carbon dioxide and the evolved permanent gas, collected over aqueous caustic potash, was analysed and found to consist solely of nitrogen. Hydrogen either free or combined could not be detected. The weight of nitrogen from one molecular proportion of diazoamino-*p*-toluene (225 g.) was 25.8 g.

This experiment was repeated, a much larger amount (4.4 g.) of diazoamine being used. A 500 c.c. gas-holder was converted into a nitrometer, and a guard-tube, packed with dry paraffin wax to remove traces of *p*-toluidine, was inserted between the graduated receiver and the acid flask in which the ammonia was fixed as chloride. The toluene and nitrogen were measured directly, the ammonia was estimated as chloroplatinate: 225 g. of diazoamine furnished 46.5 g. of toluene, 0.31 g. of ammonia, and 26.6 g. of nitrogen, these numbers corresponding approximately with the molecular ratios of 0.5 C₇H₈, 0.02 NH₃ and 0.94 N₂.

II. *Less Volatile Products of Pyrolysis.*—In earlier experiments the whole melt was distilled under reduced pressure, but experience showed that a preliminary extraction with petroleum was preferable. From two melts made by pyrolysis of 200 g. of diazoamine and 500 g. of *p*-toluidine, 482 g. of the base were recovered by distillation under reduced pressure, and when the black residue (142 g.) was extracted with excess of petroleum (b. p. 60—80°) approximately 30 g. of tarry matter remained undissolved. From this pitch a considerable amount of acid-soluble resinamine was obtained which when applied to wood surfaces from alcoholic solution gave a reddish-brown stain similar in appearance to that from the resinamines of low-temperature tar. After removal of the solvent a dark red residue (110 g.) was distilled under reduced pressure. A fraction, b. p. 74°/4 mm., consisted mainly of *p*-toluidine (22 g.), so the

whole of this base originally employed was accounted for in the distillates. The less volatile products were now distilled over a range 155—170°/4 mm., a bright red semi-solid product (57 g.) being obtained, mainly between 162° and 167°. This fraction was extracted with excess of warm 0.5*N*-hydrochloric acid; when the brownish-red residue (16 g.) was stirred with 50 c.c. of ether, 9 g. of red crystalline azo-*p*-toluene, m. p. 144° after one crystallisation from ligroin, remained undissolved. Removal of solvent from the ethereal extract yielded a semi-solid mass which gave from alcohol small characteristic red crystals of azo-*p*-toluene (1 g.) mixed with long silky needles. The less soluble azo-*p*-toluene was removed by warming the solution to 40° and filtering it rapidly; on cooling, silky yellowish-white needles (3 g.), m. p. 79°, separated from the filtrate. This product was identified as di-*p*-tolylamine and yielded a nitrosoamine crystallising from dilute alcohol in yellow needles, m. p. 101°.

6-Amino-3 : 4'-dimethylazobenzene. This substance, the chief product in the transformation of diazoamino-*p*-toluene by concentrated acid, is formed only in small quantity in the pyrolysis. Its presence could be detected in the alcoholic di-*p*-tolylamine-azo-*p*-toluene mother-liquor by a characteristic green coloration with concentrated hydrochloric acid.

In one experiment, however, a larger yield was obtained: the distillate from a melt made by pyrolysis of 267 g. of diazoamine in *p*-toluidine left after extraction with hydrochloric acid a dark brown residue (27 g.). When dry, this material was lixiviated with petroleum (b. p. 80—100°) to yield a red solution which on concentration furnished 6 g. of azo-*p*-toluene. The portion insoluble in petroleum dissolved in alcohol containing hydrochloric acid to a dark green solution, which deposited matted yellow needles (9 g.), darkening at 160° and melting at 174° (Found: Cl, 13.2, 13.5. $C_{14}H_{15}N_3 \cdot HCl$ requires Cl, 13.5%). From this *hydrochloride*, which was hydrolysed even by water, *aminoazotoluene* was liberated by warm aqueous alkali; it crystallised from petroleum (b. p. 60—80°) in lustrous red needles, m. p. 118° (Found: N, 19.3. $C_{14}H_{15}N_3$ requires N, 18.8%).

Isomeric Aminoditolyls.—The aqueous hydrochloric acid solution of primary bases (from 200 g. of diazoamino-*p*-toluene) deposited on cooling 10 g. of a hydrochloride (A) in small, thick, slightly yellow-tinted needles. Evaporation of the solution yielded a further 20 g. of these crystals. The filtrate on vigorous stirring gave a small precipitate of a hydrochloride (B) crystallising in characteristic silky needles, darkening on exposure, m. p. 175—177°, and the mother-liquor slowly furnished pale yellow, elongated plates (C), m. p. 172°.

The products B and C, which were only obtained in small amounts, yielded the same acetyl and azo- β -naphthol derivatives. They were respectively the anhydrous and the hydrated form of the same hydrochloride (Found for B : C, 70.6; H, 7.2; N, 6.0; Cl, 14.7. $C_{14}H_{15}N, HCl$ requires C, 71.9; H, 6.9; N, 6.0; Cl, 15.2. Found for C : C, 66.2; H, 7.6; N, 6.0; Cl, 13.9. $C_{14}H_{15}N, HCl, H_2O$ requires C, 66.8; H, 7.2; N, 5.6; Cl, 14.1%).

The *acetyl* compound crystallised from petroleum (b. p. 80—100°) or alcohol in colourless lustrous needles, m. p. 169.5—170.5° (Found : C, 80.0; H, 7.3; N, 6.1. $C_{16}H_{17}ON$ requires C, 80.3; H, 7.1; N, 5.9%).

The *azo- β -naphthol* derivative crystallised from benzene, containing a little alcohol, in scarlet needles, m. p. 188—189.5° (Found : C, 81.25; H, 5.9; N, 8.2. $C_{24}H_{20}ON_2$ requires C, 81.8; H, 5.7; N, 8.0%).

The small proportion of this aminoditolyl isolated did not permit of orientation experiments, but the more plentiful hydrochloride (A) yielded an isomeric base which was identified as follows:—

2-Amino-4' : 5-dimethyldiphenyl (4' : 5-dimethyl-2-xenylamine). The hydrochloride (A), recrystallised from alcohol containing hydrochloric acid, separated in colourless needles, decomp. 216—226° (Found : N, 6.1; Cl, 15.0. $C_{14}H_{15}N, HCl$ requires N, 6.0; Cl, 15.2%). This salt was readily diazotisable and treatment of the diazo-solution with sodium azide furnished an oily triazo-compound. The free base boiled at 165—167°/4 mm.

2-Acetamido-4' : 5-dimethyldiphenyl (acetyl-4' : 5-dimethyl-2-xenylamine), prepared by the action of acetic anhydride and anhydrous sodium acetate on the foregoing hydrochloride, was only very sparingly soluble in water and crystallised from petroleum (b. p. 80—100°) in rosettes of brittle colourless needles, melting at 104° and dissolving readily in alcohol, benzene or chloroform (Found : N, 6.0. $C_{16}H_{17}ON$ requires N, 5.9%).

4' : 5-Dimethyldiphenyl-2-azo- β -naphthol (4' : 5-dimethylxenyl-2-azo- β -naphthol) crystallised from benzene, containing a little alcohol, in lustrous red needles, m. p. 179.5° (Found : N, 7.95. $C_{24}H_{20}ON_2$ requires N, 8.0%). This substance was almost insoluble in the alcohols, petroleum, chloroform or acetone, but dissolved readily in glacial acetic or concentrated sulphuric acid, developing with the latter a violet-red coloration.

III. *2 : 6-Dimethylcarbazole*.—(1) *From 4' : 5-dimethyl-2-xenylamine*. This oily base was heated in a hard glass tube in a current of air so that the gases passed over glowing quicklime (compare Blank, *Ber.*, 1891, **24**, 306). An oily distillate (about 60%) was collected which rapidly solidified and was freed from a small amount of

unchanged primary base by crystallisation from benzene; 2 : 6-dimethylcarbazole then separated as a colourless solid, m. p. 224° (Found : C, 85.9; H, 6.55; N, 7.5. C₁₄H₁₃N requires C, 86.1; H, 6.65; N, 7.2%).

(2) *From azo-p-toluene.* This azo-compound was reduced with zinc and glacial acetic acid to hydrazo-*p*-toluene, which was transformed in alcoholic solution with stannous chloride and hydrochloric acid into the stannichloride of the *o*-semidine, 2-amino-4' : 5-dimethyldiphenylamine (Täuber, *Ber.*, 1892, **25**, 1023). This readily oxidisable base was set free from the tin salt by alkali and extracted with ether, and the extract dried over anhydrous sodium sulphate. The base obtained after removal of ether crystallised from petroleum (b. p. 60—80°) in shining leaflets, m. p. 107°. Conversion into triazole was best effected by ethyl nitrite in alcoholic sulphuric acid; the product precipitated by dilution with water crystallised from petroleum in brownish-white plates, m. p. 93°. When maintained for some time at 360°, this triazole yielded 2 : 6-dimethylcarbazole (Ullmann, *loc. cit.*), which was purified by crystallisation from alcohol (with charcoal) and through its picrate (m. p. 162°).

(3) *From 3-methylcyclohexanone and p-tolyldiazine.* In this synthesis both the racemoid 3-methylcyclohexanone and its dextrorotatory component were employed, the latter being obtained by hydrolysis of pulegone with sulphuric acid.

With *p*-tolyldiazine the racemoid ketone gave a hydrazone liquid at the ordinary temperature, whereas the *d*-ketone gave a solid hydrazone (m. p. about 90°). On ring closure, both hydrazones gave a crystalline dimethyltetrahydrocarbazole of m. p. 147° (sintering at 135°), although this compound still retains the asymmetric carbon atom. In either case Perkin and Plant's method for tetrahydrocarbazole was employed (J., 1921, **119**, 1831) in which the hydrazone was warmed with five parts of glacial acetic acid. A vigorous reaction ensued and the tetrahydro-compound separated; after recrystallisation from alcohol it was dehydrogenated by boiling with sulphur in quinoline (Perkin and Plant, J., 1923, **123**, 694). The product was poured into hydrochloric acid, and the crude 2 : 6-dimethylcarbazole purified by sublimation with powdered iron at 225—240° under 15—20 mm. pressure and by crystallisation from benzene. The blue fluorescence in alcohol described by Borsche (*loc. cit.*) is not shown by solutions of the purified carbazole.

The three preparations of 2 : 6-dimethylcarbazole were shown to be identical by their consistent mixed melting points of 224°.

9-Nitroso-2 : 6-dimethylcarbazole was prepared by treating a solution of 0.8 g. of 2 : 6-dimethylcarbazole in 15 c.c. of glacial

acetic acid with a slight excess of sodium nitrite (0.6 g.) in water. The solution filled with yellow felted needles, m. p. 113° after recrystallisation from spirit.

The following table gives a comparison of the properties of carbazole (m. p. 238°), 2 : 6-dimethylcarbazole (m. p. 224°), and its 3 : 6-isomeride (m. p. 219°) (Täuber and Loewenherz, *Ber.*, 1891, **24**, 1035, 2598).

Reaction.	Carbazole.	2 : 6-Dimethyl- carbazole.	3 : 6-Dimethyl- carbazole.
Picrate	M. p. 187°	M. p. 162°	M. p. 192°
Sulphuric acid with one drop of nitric acid	Blue	Yellowish-brown	Yellowish-brown
Benzoquinone in acetic acid on successive treatment with concentrated sulphuric acid, water and ether	Magenta, pale red extract	Magenta, pale red extract	Indigo-blue, blue flakes
Isatin in concentrated sulphuric acid	Indigo-blue	Indigo-blue	Indigo-blue
Chromium trioxide in sulphuric acid	Deep blue	Deep blue	No coloration
<i>p</i> -Nitrosophenol in concentrated sulphuric acid	Blue	Blue	—
9-Nitroso-compounds	M. p. 82°	M. p. 113°	M. p. 106°
Sulphuric acid with one drop of nitric acid.	Deep green, changed to blue.	Brown-red, deepened.	—
Hydrochloric acid to alcoholic solution (a); on warming (b)	(a) Red coloration (b) Blue flocks	(a) Indistinct coloration (b) Blue flocks	— —

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