349. *The Rearrangement of the Alkylanilines. Part V. Trimethylethylene, the Intermediate Product in the Rearrangement of* iso*Amylaniline Hydrobromide to* p-*Amino*-tert.-*amylbenzene Hydrobromide.*

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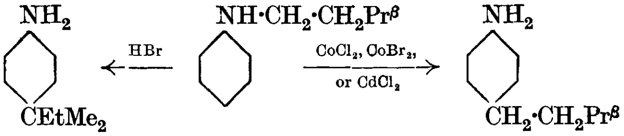
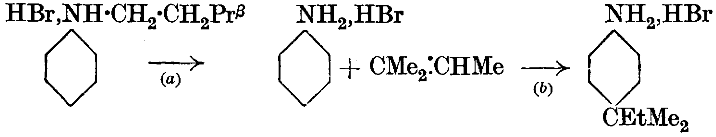
The rearrangement of *iso*butylaniline hydrobromide can be made to yield either *p*-amino-*tert.*-butylbenzene or *p*-amino*iso*butylbenzene under suitable conditions (Hickinbottom and Preston, J., 1930, 1566). It has now been found that the hydrobromide of *iso*amylaniline (I) yields *p*-amino-*tert.*-amylbenzene (III) on rearrangement. The isomerisation of the free amine at 212° in presence of cadmium chloride produces primary amines containing 98% of *p*-amino*iso*amylbenzene (II); at the same temperature, with cobalt chloride or bromide as the promoter, the product contains 2—3% of aniline and about 5% of a primary amine, b. p. above 290°, which cannot be an aminoamylbenzene: there is no evidence that the alkyl group undergoes isomerisation during its transference from nitrogen to the nucleus.



(III.) (I.) (II.)

During the rearrangement of *iso*amylaniline hydrobromide produced by 6—8 hours' heating at 240—280°, the *iso*amyl group suffers isomerisation to *tert.*-amyl: the amount of *p*-amino-*tert.*-amylbenzene (III) in the primary amines obtained is 25—45%; aniline is the principal product and trimethylethylene is also formed.

As *iso*amylaniline hydrobromide, when heated at 302°, yields trimethylethylene in large quantity (Hickinbottom and Ryder, J., 1931, 1281), the effect of heating this hydrocarbon with aniline hydrobromide in a sealed tube was investigated: under conditions strictly comparable with those required for the rearrangement of *iso*amylaniline hydrobromide, the product was *p*-amino-*tert.*-amylbenzene (III). There seems to be no reasonable doubt, therefore, that the formation of *p*-amino-*tert.*-amylbenzene from *iso*amylaniline hydrobromide is due—in a large measure at least—to the intermediate formation of trimethylethylene:



This conclusion is based on the experimental realisation of each phase of this scheme and is in accord with the fact that trimethylethylene is present in all products in which the reaction has not gone to completion, as demanded by the relative speeds of the two reactions—(*b*) the slower, (*a*) the faster.

Although the rearrangement of *iso*amylaniline hydrobromide depends on the intermediate formation of trimethylethylene, the isomerisation of *iso*amylaniline promoted by metal salts follows a different course (compare Hickinbottom and Preston, *loc. cit.*), for it is now found that this olefin reacts with aniline and cobalt chloride or bromide to give *p*-amino-*tert.*-amylbenzene, instead of *p*-amino*iso*amylbenzene. This result refutes the suggestion of Bennett and Chapman (*Ann. Reports,* 1930, 124) that the same intermediate is produced during the rearrangement of the hydrobromide and of the amine with metal salts (see also Hickinbottom and Ryder, *loc. cit.*).

Bennett and Chapman explain the rearrangement of the alkylanilines in presence of metal salts by assuming the intermediate formation of alkyl halide. This hypothesis had already been advanced in a somewhat more general form by Hickinbottom and Waine, who found it impossible to reconcile it with the experimental facts (J., 1930, 1559).

EXPERIMENTAL.

Rearrangement of iso*Amylaniline with Metal Salts as Promoters : Formation of* p-*Amino*iso*amylbenzene.*—The *iso*amylaniline used (Hickinbottom and Ryder, *loc. cit.*) had b. p. 253—254°/751 mm. (corr.) and formed a m-*nitrobenzenesulphonyl* derivative, white asbestos-like needles, m. p. 104—105°, from EtOH (Found : N, 8·15. $C_{17}H_{20}O_4N_2S$ requires N, 8·0%).

The amine (9·2 g.) was heated with anhyd. $CoCl_2$ (5 g.) for 7 hrs. at 240—250° in a long-necked flask closed with a guard-tube of soda-lime. The greenish cryst. product was treated with NH_3 aq. and extracted with Et_2O and the primary amines present in the extract were separated as sparingly sol. zincichlorides (7·96 g.) (compare Hickinbottom, J., 1930, 992), corresponding to a yield of approx. 60%. These amines were regenerated, and acetylated in aq. suspension, giving an acetyl compound, m. p. 115—115·5° after crystalln. from EtOH (Found : N, 7·05%).

The same acetyl compound was obtained from the products of other similar expts. in which $CoBr_2$ or $CdCl_2$ was used as promoter at temps. between 210° and 280°.

The amine regenerated from the acetyl derivative had b. p. 262—264°/756 mm. (corr.) and formed a benzoyl derivative, thin plates, m. p. 151—153°, from MeOH (Willgerodt and Dammann, *Ber.*, 1901, **34**, 3678, record *p*-amino*iso*amylbenzene, b. p. 256—258° ; acetyl derivative, m. p. 113—114° ; benzoyl derivative, m. p. 147° ; compare also Calm, *Ber.*, 1882, **15**, 1642 ; Anschütz and Beckerhoff, *Annalen*, 1903, **327**, 218). The acetyl and the benzoyl derivative depressed the m. p.'s of the corresponding derivatives of *p*-amino-*tert.*-amylbenzene, but not those of the derivatives of *p*-amino*iso*amylbenzene prepared by the methods of Willgerodt and Dammann and of Calm.

p-Amino*iso*amylbenzene formed a m-*nitrobenzenesulphonyl* derivative, m. p. 99—101° (Found : N, 8·3. $C_{17}H_{20}O_4N_2S$ requires N, 8·0%), and gave with phenyl *iso*thiocyanate p-iso*amyldiphenylthiourea*, small nodules, m. p. 122°, from EtOH (Found : N, 9·6. $C_{18}H_{22}N_2S$ requires N, 9·4%).

A series of expts. was made with the object of ascertaining the yield of p-amino*iso*amylbenzene and the relative amount of other products. *iso*Amylaniline was heated (vapour from boiling ethyl benzoate) with anhyd. metal chloride for a definite time in a long tube having a pear-shaped bulb blown at the lower end, the other end being open to the atmosphere through guard-tubes containing $CaCl_2$ and $Mg(ClO_4)_2$. The product was dissolved in warm dil. HCl and the amines were liberated by NH_3 aq. As the impurities in the *p*-amino*iso*amylbenzene amounted to only a few units %, it was necessary not only to estimate and separate small amounts of aniline, but to develop a method capable of detecting, and if necessary of estimating, small quantities of isomeric aminoamylbenzenes. A slight excess of 50% $ZnCl_2$ aq. was added to the amines liberated from the reaction product, and the paste formed was thoroughly ground and kept over-night. The insol. zincichlorides were collected in a sintered glass funnel, washed with H_2O, and extracted several times with boiling light petroleum (b. p. 60—80°) to remove secondary amine completely (the presence of traces of this leads to unsatisfactory results in the subsequent assay). From the zincichlorides, dried to const. wt. at 100°, the yield of primary amines can be calculated. The approx. amount of aniline in the primary amines thus pptd. was determined by decomposing the zincichlorides with NH_3 aq., removing the liberated amines in Et_2O, washing (H_2O), drying (Na_2SO_4), and evaporating the extract, acetylating the residue by evaporation with an aq. suspension of Ac_2O, and drying the product to const. wt. in a steam-oven; a weighed amount of this product was boiled with 20—30 times its wt. of H_2O and, after cooling, the insol. acetyl compound was collected and dried. Evaporation of the aq. extract gave the wt. of crude acetanilide, from which the wt. of aniline recorded in col. 6 of the table was calculated. The m. p. of the residue of acetyl derivative after extraction, recorded in col. 7, gives a rough measure of the purity of the principal product (*p*-*iso*amylacetanilide, m. p. 115·5°. The m. p. recorded here is the temp. at which the last trace of solid liquefied). The impurity remaining in this product was acertained by hydrolysis of the crude acetyl compound from a number of expts., and fractionation of the amines thus obtained. *p*-Amino*iso*amylbenzene, b. p. 262—264° (corr.), was the principal product. A primary amine, b. p. above 290°, amounting to about 5% of the total wt. of amines was obtained: it is being examined, but it is evident that it cannot be an isomeride of amino*iso*amylbenzene. Search was made for amino-*tert.*-amylbenzene in the fractions collected up to 262°. Each was acetylated separately by evaporation to dryness with an aq. suspension of Ac_2O, and the crude acetyl derivative obtained was extracted with H_2O in the manner described above, to remove acetanilide. There remained *p*-*iso*amylacetanilide without any serious amount of other compounds, for the m. p. of the extracted fractions varied between 114° and 115°. The presence of *p*-*tert.*-amylacetanilide would have been shown by the lowering of the m. p., 4% producing the quite noticeable depression of 1·5° and the m. p. of a mixture of this composition not being changed by extraction with H_2O. The total wt. of the fractions examined in this way amounted to 20% of the total wt. of primary amines, and it is concluded, therefore, that if *p*-amino-*tert.*-amylbenzene is present in the reaction product it constitutes less than 1% of the total primary amines formed.

The light petroleum extract of the zincichlorides was also examined. Repeated extraction with very dil. HCl removed unchanged *iso*amylaniline (identified by its *m*-nitrobenzenesulphonyl derivative, m. p. 104—105°) and a small quantity of *p*-amino*iso*amylbenzene which had escaped pptn. as zincichloride. There remained in the light petroleum solutions an amine having all the reactions of a nuclear-substituted diphenylamine; it boiled unchanged at 325—330° (corr.) and its solution in conc. H_2SO_4 gave a light yellow coloration on the addition of HNO_3. No simple cryst. derivative has yet been obtained from it. A rough estimation of the amount of this substance formed in each reaction was made by evaporating the light petroleum solution in a tared dish after extraction with very dil. HCl. It appears that the yield of this product increases with the length of heating and that the nature of the promoter used also has an influence.

iso-Amyl aniline, g.	Promoter, g.	Heating, hrs.	Crude amino-amylbenzene, g.	Aniline, g.	Extracted Ac cmpd., m. p.	Substd. diphenylamine, g.
4·91	$CoCl_2$ 2·75	11	2·52	0·075	111°	1·22
4·42	$CoCl_2$ 1·85	11	2·02	—	—	1·27
3·67	$CoBr_2$ 3·58	7·25	1·55	0·031	112	0·97
3·66	$CdCl_2$ 4·75	7	2·57	0·018	114·5	0·37
4·33	$CoCl_2$ 3·82	7·5	1·61	—	—	0·40

Rearrangement of iso*Amylaniline Hydrobromide : Formation of* p-*Amino*-tert.-*amylbenzene.*—The dry hydrobromide (7·95 g.), heated at 230° for 5—6 hrs. in a sealed tube, gave a layer of amylene resting on a solid mass of amine hydrobromides. The primary amines were separated as zincichlorides (4·05 g.), regenerated, and roughly separated by distillation into approx. equal amounts of aniline and aminoamylbenzene. The latter was identified as *p*-amino-*tert.*-amylbenzene by means of its acetyl derivative, m. p. 140—141° (Anschütz and Beckerhoff, *loc. cit.*, give m. p. 138—139°), alone or mixed with a specimen prepared from *p*-amino-*tert.*-amylbenzene obtained by heating *tert.*-amyl alcohol with aniline and $ZnCl_2$.

In other expts. the rearrangement of *iso*amylaniline hydrobromide at temps. between 220° and 280° invariably produced *p*-amino-*tert.*-amylbenzene and no serious quantity of any isomeric amine.

Reaction of Trimethylethylene with Aniline : Formation of p-*Amino*-tert.-*amylbenzene.*—(a) *With aniline hydrobromide.* Trimethylethylene was heated with dry aniline hydrobromide (2 parts) in a sealed tube at 245—250° for 5 hrs. (in other expts., at 230—240° and at 260—280°). There resulted a solid mass of amine salts covered by a layer of unchanged amylene. After treatment with alkali the liberated amines were separated by distillation into aniline (65%) and *p*-amino-*tert.*-amylbenzene (35%) (acetyl derivative, m. p. and mixed m. p. Found : N, 7·2. Calc. : N, 6·8%).

(b) *With aniline cobaltobromide or cobaltochloride.* Trimethylethylene (4 c.c.) and aniline cobaltobromide (10 g.) were heated in a sealed tube at 180° for 6 hrs. The product, treated as in (a), gave aniline (1·3 g.), *p*-amino-*tert.*-amylbenzene (2·9 g., identified as its acetyl derivative), and a semi-resinous residue (0·45 g.). The same products were obtained after aniline cobaltochloride (12·7 g., free from EtOH) (Lippmann and Vortmann, *Ber.*, 1878, **11**, 1069; Percival and Wardlaw, J., 1929, 1318) and trimethylethylene (2·6 g.) had been heated in a sealed tube for 6 hrs. at 240—250°.

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