CLXIX.—*The Rearrangement of the Alkylanilines. Part IV. The Formation of Olefins from the Alkylaniline Hydrobromides.*

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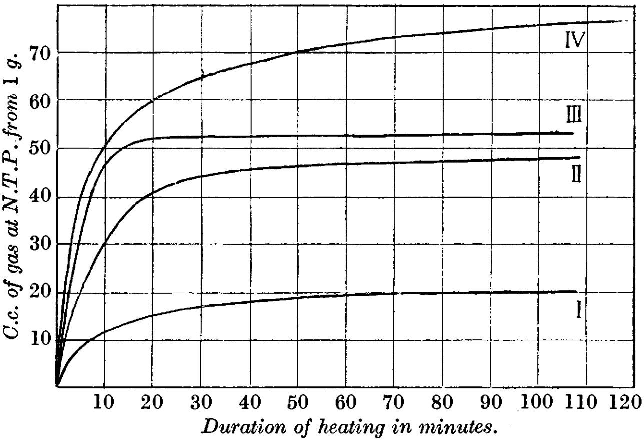
Hickinbottom and Preston (J., 1930, 1566) have shown that the product of the rearrangement of *iso*butylaniline is dependent on the nature of the catalyst promoting the change; the use of metal halides gives *p*-amino*iso*butylbenzene, whereas halogen hydrides produce *p*-amino-*tert.*-butylbenzene.

It appeared that some indication of the cause of this striking difference would be furnished by a closer examination of the behaviour of the halogen hydride salts of the alkylanilines when heated. This paper records observations on the products formed when the hydrobromides are maintained between 238° and 302° so that the volatile products may be collected continuously and examined.

The hydrobromides of ethyl-, *n*-propyl-, *n*-butyl-, *iso*butyl-, and *iso*amyl-anilines decompose into olefin and alkyl bromide, the relative proportions of the two volatile products being dependent on the temperature and on the nature of the alkyl group. In columns 12 and 13 of Table I are given the percentages of the alkyl group present in the product as olefin and as alkyl bromide. It is evident that in ascending the series from ethylaniline to *iso*amylaniline there is a progressive increase in the proportion of olefin in the volatile products of decomposition. This is illustrated by the curves in Fig. 1, which give the volumes of gas, corrected to N.T.P., evolved from 1 g. of hydrobromide heated at 302°. The curves show that the evolution of the olefin is comparatively rapid, the greater part being collected during the first half hour of heating.

FIG. 1.



I. *Ethylaniline hydrobromide.* II. n-*Propylaniline hydrobromide.*
III. n-*Butylaniline hydrobromide.* IV. iso*Butylaniline hydrobromide.*

The olefins were identified by the preparation of their dibromides, ethylene and *n*-butylene being further characterised by the formation of the corresponding diarylamino-compounds. *n*-Butylaniline hydrobromide yielded β-butylene, $CH_3{\cdot}CH{:}CH{\cdot}CH_3$, a mode of decomposition which resembles the dehydration of *n*-butyl alcohol by sulphuric acid (compare Young and Lucas, *J. Amer. Chem. Soc.*, 1920, **52**, 1962).

Although the elimination of an alkyl group from quaternary ammonium compounds as olefin is well known (compare Hanhart and Ingold, J., 1927, 997), there does not appear, as far as the authors are aware, to be any previous record of the breakdown of the alkylaniline salts to give olefin.

The reaction is not confined to the elimination of the alkyl group as olefin and alkyl bromide. The non-volatile portion of the product was found to contain, in addition to aniline and the secondary amine,

TABLE I.

Hydrobromide.	Wt., g.	Temp.	Series	Time, hrs.	Olefin, c.c. at N.T.P.	Olefin, g.	Bromidion, g., before heating.	Bromidion, g., after heating.	Alkyl bromide, g.	Amino-alkyl-benzene, g.	% Alkyl group as olefin.	% Alkyl group as alkyl bromide.	% Alkyl group as aminoalkyl-benzene.
Ethylaniline	4·8455	302°	b	2	76·03	0·0958	1·9168	1·5518	0·4977	1·52	14·3	19·1	52·3
	5·0586	302	b	2	84·54	0·1066	2·0010	1·5941	0·5548	0·71*	15·2	20·3	23·4
	5·7351	302	b	4	92·50	0·1166 [1]	2·2686	1·8060	0·6307	—	14·7	21·6	—
n Propylaniline	2·2345	302	b	2	84·35	0·1584 [2]	0·8304	0·6545	0·2707	—	37·3	21·3	—
	2·1910	302	b	2	81·69	0·1534	0·8105	0·6375	0·2662	0·21	36·0	21·4	15·6
	1·6068	302	a	2·75	67·2	0·1262	0·5795	0·4498	0·1996	—	40·4	21·8	—
n-Butylaniline	2·2034	302	b	2	110·8	0·2770 [3]	0·7654	0·6677	0·1675	—	51·6	12·8	—
	2·2000	302	b	2	107·4	0·2685	0·7642	0·6383	0·2158	—	50·1	16·5	—
	1·6393	302	a	2	87·4	0·2185	0·5695	0·4604	0·1870	—	54·7	19·2	—
	1·8120	302	a	2	89·2	0·2235	0·6294	0·4766	0·2619	—	50·6	19·8	—
	2·1398	270	a	2	106·7	0·2667	0·7743	0·6022	0·2950	0·088	51·2	23·0	3·6
	1·6682	270	a	2	78·3	0·1958	0·5759	0·4498	0·2223		48·2	22·4	
	3·1956	238	a	3	—	—	0·9716	0·8196	—	0·251	—	—	12·4
	1·6136	238	a	3	40·5	0·1013	0·5697	0·4388	0·2243	—	25·8	23·3	—
	1·6114	238	a	3	36·35	0·0909	0·5598	0·4268	0·2280	—	23·2	23·8	—
*iso*Butylaniline	2·3802	302	b	2	163·3	0·4083	0·8275	0·7575	0·1200	—	70·4	8·5	—
	1·9964	302	b	2	149·1	0·3727	0·6935	0·6655	0·0480	—	76·6	4·1	—
	1·5862	302	a	2	97·85	0·2446	0·5512	0·5267	0·0420	0·11	64·8	4·6	3·0
	1·6304	302	a	2	97·05	0·2426	0·5618	0·5259	0·0615		61·1	6·3	
	1·7457	302	a	2	106·7	0·2667	0·6062	0·5336	0·1244		62·7	12·0	
	1·6851	302	a	2	105·7	0·2642	0·5851	0·5418	0·0742		64·3	7·4	
	1·4852	270	a	2	67·8	0·1695	0·5161	0·4749	0·0706	0·57	46·8	8·0	29·0
	1·5371	270	a	2	65·3	0·1633	0·5465	0·4800	0·1140		45·3	12·5	
	1·5551	238	a	3	51·5	0·1287	0·5404	0·4842	0·0967	1·27	34·0	10·5	44·0
	1·4547	238	a	3	43·5	0·1089	—	—	—		36·1	—	
	1·4082	238	a	3	—	—	0·4894	0·4290	0·1035		—	12·3	
*iso*Amylaniline	3·5616	302	b	2	—	0·7532 [4]	1·1708	1·1120	0·111	—	72·5	5·0	—

[1] 1 l. ethylene weighs 1·2604 g. at N.T.P. (Landolt–Börnstein, V, 169).
[2] 1 l. propylene weighs 1·8780 g. at N.T.P. (*ibid.*).
[3] 1 l. butylene assumed to weigh 2·50 g. at N.T.P.

The amylene was determined, after collection in ice-cold carbon tetrachloride, by titration with bromine in carbon tetrachloride which had been standardised against a pure sample of *iso*amylene.

the corresponding *p*-aminoalkylbenzene (compare Hickinbottom, J., 1927, 64).

Bennett and Chapman (*Ann. Reports*, 1930, 124) have attempted to account for the rearrangement of *iso*butylaniline hydrobromide to *p*-amino-*tert.*-butylbenzene (Hickinbottom and Preston, *loc. cit.*) by the suggestion " that the hydrobromide evolved rapidly a large proportion of *iso*butyl bromide, which isomerised to the tertiary halide in the vapour phase before recombination." It is not clear what is the experimental basis for this suggestion, for there has been no previous record, as far as the authors are aware, of the thermal decomposition of *iso*butylaniline hydrobromide. It appears to be a special application of a hypothesis based on the decomposition of phenyltrimethylammonium iodide (Michael, *Ber.*, 1881, **14**, 2107, footnote).

It is evident from the experimental results given in Table I that *iso*butylaniline hydrobromide does not rapidly evolve " a large proportion of *iso*butyl bromide." Indeed, *iso*butyl bromide is only a minor product of the decomposition; under the most favourable conditions about 12% of the butyl group is evolved as bromide, but usually the proportion is lower. Even if it is shown subsequently that *iso*- and *tert.*-butyl bromides can react with the nucleus of aniline under the conditions usually obtaining during rearrangement, the bromide liberated on heating can account for only a small amount of the rearrangement.

The butyl bromide evolved has been found to consist very largely of the *iso*-bromide. Yet while this is being evolved there is a simultaneous transference of the butyl group to the nucleus, *p*-amino-*tert.*-butylbenzene being formed as a consequence of the butyl group undergoing isomerisation during the migration from the nitrogen to the ring.

It must be concluded that the explanation of Bennett and Chapman is at variance with the ascertained facts, and fails completely to account for the production of *p*-amino-*tert.*-butylbenzene from *iso*butylaniline hydrobromide. It will be shown in a subsequent paper that there is satisfactory evidence for assuming that olefins can take part in the transference of the alkyl group from nitrogen to the nucleus.

EXPERIMENTAL

The Products of Thermal Decomposition of the Alkylaniline Hydrobromides.—The hydrobromide was heated in a flask at 302° or other suitable temperature. The volatile products were passed through two short condensers and the alkyl bromide thus condensed was collected in a receiver at 0°. The uncondensed gases were passed into a flask, cooled by ice-water, containing bromine vapour, which was maintained in slight excess by suitable additions of the halogen. The volatile products from *iso*amylaniline hydrobromide could be condensed without difficulty and later separated by fractional distillation.

Ethylaniline hydrobromide (302°, 2 hours) gave ethyl bromide, b. p. 35—40°, characterised by conversion into *p*-bromophenylethylnitrosoamine, which separated from light petroleum in colourless crystals, m. p. and mixed m. p. 62—63° (Meldola and Streatfeild, J., 1889, **55**, 423, describe the nitrosoamine as separating from aqueous alcohol in lustrous ochreous plates, m. p. 63—64°).

The gas evolved in the decomposition was identified as ethylene by conversion into the dibromide, b. p. 126—130°, and then, by reaction of the dibromide with aniline, into a mixture of 1 : 4-diphenylpiperazine, m. p. and mixed m. p. 160—161°, and *s*-diphenylethylenediamine, characterised by its nitrosoamine, m. p. 158—159°.

The non-volatile decomposition product was found to contain *p*-aminoethylbenzene by the isolation of its sulphate and then by formation of its acetyl derivative, m. p. and mixed m. p. 93—94°.

n-Propylaniline (J., 1930, 992) was purified by the crystallisation of its hydrobromide from alcohol.

The hydrobromide (302°, 1 hour) gave propylene (dibromide, b. p. 138—142°), and *n*-propyl bromide, b. p. 68—72°, characterised by conversion into *n*-propylacetanilide, m. p. and mixed m. p. 47—49°. *p*-Aminopropylbenzene was isolated from the non-volatile residue and characterised by its acetyl derivative, m. p. 102—103°.

n-Butylaniline hydrobromide (302°, 1 hour) gave *n*-butyl bromide, identified by conversion into *p*-toluenesulphonphenyl-*n*-butylamide, m. p. and mixed m. p. 55—56° (von Braun and Murjahn, *Ber.*, 1926, **59**, 1202, give m. p. 54°).

The olefin evolved during the decomposition gave a dibromide, b. p. 155—158°, having the constants of βγ-dibromobutane (αβ-dibromobutane, b. p. 165—166°; βγ-dibromobutane, b. p. 158° or 161°). It was characterised as βγ-dibromobutane by converting it into *dl*-βγ-di-*p*-tolylaminobutane, m. p. and mixed m. p. 60—62° (picrate, m. p. and mixed m. p. 169°), and *meso*-βγ-di-*p*-tolylaminobutane, identified by its sparingly soluble hydrochloride and its nitrosoamine, m. p. 143—145° (Morgan and Hickinbottom, J., 1923, **123**, 97; Morgan, Hickinbottom, and Barker, *Proc. Roy. Soc.*, 1926, *A*, **110**, 505). The proportion of the *meso*-amine in the product from the dibromide was small.

From the non-volatile decomposition product, *p*-amino-*n*-butylbenzene was isolated through its sulphate; it was characterised by its acetyl derivative, m. p. and mixed m. p. 95—98°. There was distinct evidence of the presence of an isomeric aminobutylbenzene in the crude product, and this point is being investigated.

iso*Butylaniline hydrobromide.* An improvement in the method previously described for the preparation of *iso*butylaniline consists in using the *iso*butyl iodide. The yield of approximately pure *iso*butylaniline from 72 g. of iodide was 30 g. (theoretical, 62 g.).

*iso*Butylaniline hydrobromide (30 g.) was heated in an oil-bath at 240—270°. The fused salt effervesced vigorously and solidified after 25 minutes; the heating was then discontinued. The butyl bromide collected during this period distilled between 85° and 93°, the greater part at 89—93° (yield, 0·77 g.) (*iso*butyl bromide, b. p. 92°; *tert.*-butyl bromide, b. p. 72°). It was characterised by the formation of *p*-toluenesulphonphenyl*iso*butylamide, m. p. and mixed m. p. 123°.*

The olefin evolved in the decomposition, on treatment with bromine, gave dibromo*iso*butane, b. p. 148—149°, together with smaller amounts of a fraction, b. p. 80—100°, and a fraction boiling much above 180°. Linnemann and Zotta (*Annalen*, 1872, **162**, 36) and Pogorschelski (*J. Russ. Phys. Chem. Soc.*, 1905, **36**, 1486) found that pure *iso*butylene on conversion into dibromide gave in addition appreciable quantities of a tribromide and some butyl bromide.

From the non-volatile decomposition product, *p*-amino-*tert.*-butylbenzene was isolated, b. p. 225—230° (uncorr.); acetyl derivative, m. p. and mixed m. p. 169—170°.

Decomposition of *iso*butylaniline hydrobromide at 302° gave the same products.

iso*Amylaniline hydrobromide.* *iso*Amylaniline was prepared by the general method previously described (Hickinbottom, J., 1930, 992). 85 G. of crude *iso*amylaniline, b. p. 245—255° (uncorr.)—the greater part distilled at 246—248° (uncorr.)—was obtained from 133 g. of *iso*amyl iodide (theoretical, 109 g.). It was purified by crystallisation of its *hydrobromide* from benzene or alcohol (Found : HBr, 32·9. $C_{11}H_{17}N,HBr$ requires HBr, 32·7%). The hydrobromide, m. p. 148—151°, is readily soluble in warm benzene and alcohol or cold chloroform. The hydrochloride separates from carbon tetrachloride in clusters of small needles, m. p. 148—150°; the *p*-toluenesulphonyl derivative forms flattened prisms, m. p. 79—80°, from alcohol (von Braun and Murjahn, *loc. cit.*, give hydrochloride, m. p. 151°; *p*-toluenesulphonyl derivative, m. p. 81—82°).

*iso*Amylaniline hydrobromide heated at 240—270° during 1 hour gave *iso*amylene, b. p. 38—40°, and *iso*amyl bromide, b. p. 115—

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* In a previous paper (J., 1930, 994) the authors described this compound without being aware that von Braun and Murjahn (*loc. cit.*) had prepared it previously and found m. p. 121°.

120°. From the residue, *p*-amino-*tert.*-amylbenzene was isolated; acetyl derivative, m. p. 134° (Willgerodt and Dammann, *Ber.*, 1901, **34**, 3678, give m. p. 138—139°; the isomeric *iso*amyl compound has m. p. 113—114°).

Estimation of the Products formed in the Decomposition of the Alkylaniline Hydrobromides.—The apparatus consisted of a tube having a small bulb (A) blown at one end and inclined at a few degrees from the horizontal. It was sealed to a short condenser, the lower end of which was sealed into the ground-in cap of a cooled receiver. This cap also carried a second and similar condenser to trap any uncondensed vapours leaving the receiver. The uncondensed gas was collected over potassium hydroxide solution in a nitrometer, from which it was periodically transferred to a gas burette for analysis. The bulb (A) served to hold the amine hydrobromide, which was heated to a constant temperature by a surrounding vapour bath. The vapours of the following substances were used: diphenylamine, b. p. 302°; amyl salicylate, b. p. 270°; quinoline, b. p. 238°.

In one series of experiments—designated (a)—the whole of the apparatus was filled with dried carbon dioxide, and the olefin swept out, as it was liberated, by a gentle stream of dry carbon dioxide. In another set of experiments—(b)—the apparatus was initially full of air, and carbon dioxide was introduced to sweep out the olefin after the period of heating had been completed. In this series, the gas collected in the nitrometer was measured after known intervals from the commencement of the fusion of the hydrobromide: the results furnished the data on which the curves (Fig. 1) showing the rates of evolution of olefin are based. In both series, the olefin was estimated by the usual process of gas analysis by absorption in bromine water.

The alkyl bromides could not be determined sufficiently accurately by direct weighing. The non-volatile residue was therefore dissolved in aqueous alcohol, and the bromidion in an aliquot portion estimated: from the difference between the bromidion present before heating and after, the loss of alkyl bromide was calculated.

After the determination of bromidion in the residue, the remainder of the solution was concentrated after acidification, the amines liberated, and the primary amines separated from the other products as zincichlorides. The zincichlorides were collected on a sintered funnel, and dried in order to obtain a measure of the total primary amines present. The proportion of aniline and *p*-aminoalkylbenzene was determined by liberating the amines from the zincichlorides, and converting them into hydrobromides or hydrochlorides by evaporation with the appropriate acid. An estimation of the halidion in the dried mixture of salts allowed the calculation of the relative proportions of aniline and *p*-aminoalkylbenzene. Owing to the serious effect of small experimental errors in these estimations, the amounts of *p*-aminoalkylbenzene recorded are only approximate. The experimental results are summarised in Table I.

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