CCI.—*The Rearrangement of the Alkylanilines. Part III. The Formation of* p-*Amino*iso*butylbenzene and of* p-*Amino*-tert.-*butylbenzene from* iso*Butylaniline.*

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*iso*BUTYLANILINE hydrobromide, when heated in a sealed tube at 220—300°, is converted into *p*-amino-*tert.*-butylbenzene (III) in good yield. The identity of the primary amine thus formed was established by comparison of some of its derivatives with those of *p*-amino-*tert.*-butylbenzene which had been prepared from *tert.*-butylbenzene (Senkowski, *Ber.*, 1890, **23**, 2414; Shoesmith and Mackie, J., 1928, 2334). This amine is also formed when *iso*butylaniline hydrochloride is heated in a sealed tube at 280—290°; and in small yield by heating *iso*butylaniline hydrobromide in a sealed tube with dry cobalt bromide or zinc bromide, the principal products under these conditions being aniline and a neutral oil which appears to consist largely of polymerised olefins.

The isomerisation of an alkyl group during migration from nitrogen to carbon has been recorded previously for the change of *n*-propylpyridinium iodide to *iso*propylpyridine hydriodide (Ladenburg, *Annalen*, 1888, **247**, 22), but as far as the authors are aware there is no previous record of a similar isomerisation in the benzene series.

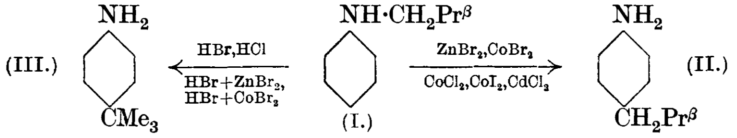
The value of the observation, however, lies in the fact that it provides a further method of determining whether or not the rearrangement of the free alkylanilines in presence of metallic salts is dependent on the intermediate formation of the hydrogen halide salts of the secondary amine through the action of traces of water (see preceding paper).

It is evident, in view of the above results, that if *iso*butylaniline hydrobromide is an intermediate product in the rearrangement of free *iso*butylaniline in presence of cobalt bromide or zinc bromide, the final products would be identical with those obtained when *iso*butylaniline hydrobromide is heated with cobalt bromide or zinc bromide. It was found, however, that dry *iso*butylaniline underwent rearrangement when heated with zinc bromide or cobalt bromide, to give an aminobutylbenzene which was quite distinct from *p*-amino-*tert.*-butylbenzene. The yield of the new primary amine is approximately 95% of the *iso*butylaniline employed when allowance is made for recovered secondary amine.

The amino- and the butyl group in the new amine were shown to be in the para-position with respect to each other by conversion of the amine through *p*-chlorobutylbenzene into *p*-chlorobenzoic acid. The configuration of the butyl group follows from the fact that the amine is not identical with any of the three known *p*-aminobutylbenzenes. It must therefore be the hitherto unknown p-*amino*iso*butylbenzene* (II). In the following table the constants of *p*-amino*iso*butylbenzene and its derivatives are compared with those of the other three isomeric *p*-aminobutylbenzenes.

Butylbenzene.	B. p.	Acetyl, m. p.	*p*-Toluene-sulphonyl, m. p.	Phenyl-thiourea, m. p.
p-Amino-*n*-	258—260°/750 mm.	105°	—	—
p-Amino-*sec*.-	238°/760 mm.	125	—	—
p-Amino*iso*-	235—236° (uncorr.)	127—128	136—137°	130—131°
p-Amino-*tert*.-	228—230° (uncorr.)	169	178	156

Although references to *p*-amino*iso*butylbenzene occur in the literature (Studer, *Annalen*, 1882, **211**, 236; Lloyd, *Ber*., 1887, **20**, 1254), it is evident from the recorded melting points of its derivatives and methods of preparation that the amine previously referred to as *p*-amino*iso*butylbenzene is actually *p*-amino-*tert*.-butylbenzene (compare Senkowski, *Ber*., 1891, **24**, 2974).



As the product of the rearrangement of *iso*butylaniline in presence of hydrogen chloride or hydrogen bromide is quite distinct from that obtained when the rearrangement of the free amine is promoted by dry metallic halides, it is evident that the isomerising action of the metallic halides is not dependent on the intermediate formation of hydrogen halide postulated in the hypothesis outlined on p. 1559. Consideration of evidence of a different nature (preceding paper) also leads to a similar conclusion, namely, that the rearrangement of the alkylanilines, when promoted by metallic salts, proceeds without the formation of any demonstrable volatile intermediate compound, such as olefin or alkyl halide. It must be concluded, therefore, in the absence of any satisfactory evidence to the contrary, that the change of the alkylanilines to *p*-aminoalkylbenzenes which occurs on heating with metallic salts is a true isomerisation.

EXPERIMENTAL.

Rearrangement of iso*Butylaniline Hydrobromide*: *Formation of* p-*Amino*-tert.-*butylbenzene*.—The *iso*butylaniline used in these experiments was prepared and purified as described previously (this vol., p. 994). It was free from primary and tertiary amines.

Dry *iso*butylaniline hydrobromide was heated in a sealed tube at 280—290° for 8 hours. The solid product after cooling was a mass of plate-like crystals having in places a distinct brownish tint; there was an escape of an inflammable gas when the tube was opened. After the product had been made alkaline and extracted with ether, the primary amines were isolated by Morgan's method of precipitating them with aqueous zinc chloride (E.P. 102834, 1916; compare this vol., p. 993). The primary amine on acetylation gave a product, m. p. 145—152°, raised to the constant value 168—169° by one crystallisation from alcohol. This acetyl compound did not depress the melting point of *p*-acetamido-*tert.*-butylbenzene prepared from *tert.*-butylbenzene by Senkowski's method (*Ber.*, 1890, **23**, 2414). The yield of primary amine obtained in the rearrangement of *iso*butylaniline hydrobromide (6·43 g.) was 3·7 g., calculated from the weight of the zincichloride, and the weight of secondary amine recovered was 0·4 g. The conversion is approximately 90%.

In another experiment, dry *iso*butylaniline hydrobromide, heated in a sealed tube for 8 hours at 270—310°, gave 76% of primary amine, determined by Hinsberg's method (*Ber.*, 1905, **38**, 906) using *p*-toluenesulphonyl chloride. The toluenesulphonyl derivative after crystallisation from alcohol melted at 179—180°, alone or mixed with *p*-toluenesulphonamido-*tert.*-butylbenzene derived from *tert.*-butylbenzene.

Rearrangement of iso*Butylaniline Hydrobromide in Presence of Metallic Salts.*—Dry cobalt bromide (4 g.) and *iso*butylaniline hydrobromide (5 g.), heated in a sealed tube at 290° for 6 hours, yielded a green solid. After solution in hydrochloric acid, dilution with water, and filtration to remove neutral oily matter, the basic product was isolated by addition of an excess of ammonia and extraction with ether. The primary amines present, freed from secondary amine by the usual treatment with aqueous zinc chloride, were acetylated. The acetyl derivatives thus formed were separated by fractional extraction with hot water into acetanilide (the major constituent), m. p. 112°, and *p*-acetamido-*tert.*-butylbenzene, m. p. 168—169°. A similar result was obtained when *iso*butylaniline hydrobromide was heated with zinc bromide.

Rearrangement of iso*Butylaniline Hydrochloride: Formation of* p-*Amino*-tert.-*butylbenzene.*—The pure dry hydrochloride (3·65 g.) was heated in a sealed tube at 280—290° for 6 hours. The primary amines (yield, 55% of the *iso*butylaniline employed) were isolated through their sparingly soluble zincichlorides and acetylated in aqueous suspension. Subsequent evaporation yielded a product,

m. p. 130—145°, and 168—169° after crystallisation from alcohol, which was then identified as *p*-acetamido-*tert.*-butylbenzene.

The low melting point of the crude acetyl derivative was not raised appreciably by extraction with hot water and was due to the presence of a second acetyl compound of similar solubility in water. This acetyl compound was formed in this experiment in comparatively small amount, but was produced in larger quantities in the experiments on the rearrangement of *iso*butylaniline hydrochloride where the temperature and the duration of heating were varied : it has not yet been isolated in a pure state.

p-*Amino*-tert.-*butylbenzene.*—*p*-Acetamido-*tert.*-butylbenzene, after several evaporations, or by boiling under reflux for 10 hours, with 20% hydrochloric acid, yielded *p*-amino-*tert.*-butylbenzene hydrochloride. The free amine, b. p. 228—230°/762 mm. (uncorr.) (Senkowski, *loc. cit.*, gives 239·4—240·4°/739 mm.), was further characterised by its p-*toluenesulphonyl* derivative, small thin plates, m. p. 179—180°, from alcohol (Found : N, 4·8. $C_{17}H_{21}O_2NS$ requires N, 4·6%). Its sodium salt is sparingly soluble in a moderate excess of 20% aqueous sodium hydroxide.

p-tert.-*Butyldiphenylthiocarbamide* separated as a white crystalline powder when phenylthiocarbimide was warmed with a slight excess of *p*-amino-*tert.*-butylbenzene in light petroleum. It crystallised from warm alcohol in small needles, frequently grouped in semi-globular aggregates, m. p. 156—157° (Found : N, 10·1. $C_{17}H_{20}N_2S$ requires N, 9·9%).

Rearrangement of iso*Butylaniline in Presence of Metallic Salts in Sealed Tubes*: *Formation of* p-*Amino*iso*butylbenzene.*—(1) *In presence of zinc bromide.* *iso*Butylaniline (3·8 g.) and anhydrous zinc bromide (2 g.) were heated in a sealed tube for 6 hours at 280—310°. The product was a greyish solid, and when the tube was opened an inflammable gas escaped. The primary amines present (1·38 g.) were separated from unchanged secondary amines by treatment with zinc chloride and acetylated in aqueous suspension with acetic anhydride. The m. p. of the crude acetyl compound (110—115°) was raised by crystallisation from alcohol to the constant value 127—128°, and this was depressed in presence of *p*-acetamido-*tert.*-butylbenzene.

(2) *In presence of cobalt bromide.* *iso*Butylaniline (3·8 g.), heated with anhydrous cobalt bromide (3 g.) at 260—270° for 6 hours, yielded primary amines (1·3 g.) consisting of *p*-amino*iso*butylbenzene (acetyl derivative, m. p. 127—128°) and a small proportion of aniline.

Further quantities of the acetyl compound, m. p. 127—128°, were obtained from other similar experiments. It separated from warm alcohol in large transparent plates, m. p. 127—128° (Found : N, 7·6. $C_{12}H_{17}ON$ requires N, 7·3%), depressed in the presence of *p*-acetamido-*sec.*-butylbenzene (Reilly and Hickinbottom, *loc. cit.*).

Hydrolysis of p-*Acetamido*iso*butylbenzene and Isolation of* p-*Amino*iso*butylbenzene.*—The purified acetyl compound, covered with concentrated hydrochloric acid, gave a white paste of the hydrochloride when warmed gently on a boiling water-bath for about a minute. On further heating, the hydrochloride dissolved, and hydrolysis of the acetyl compound was completed, after addition of more hydrochloric acid, by heating for several hours. Neutralisation with sodium hydroxide liberated p-*amino*iso*butylbenzene*, b. p. 235—236°/762 mm. (uncorr.), a very pale yellow liquid, of not unpleasant odour, which darkened only slowly on keeping. It was miscible with the common organic solvents but almost insoluble in water (Found : C, 80·4; H, 10·3; N, 9·5. $C_{10}H_{15}N$ requires C, 80·5; H, 10·1; N, 9·4%).

The *hydrochloride*, precipitated by the addition of hydrochloric acid to the amine, crystallised from warm dilute hydrochloric acid in clusters of interlaced needles (Found : Cl, 19·1. $C_{10}H_{15}N,HCl$ requires Cl, 19·1%). The *hydrobromide* was soluble in water and alcohol, but the addition of hydrobromic acid to an aqueous solution precipitated the salt in platelets (Found: N, 6·2; Br, 34·5. $C_{10}H_{15}N,HBr$ requires N, 6·1; Br, 34·7%).

The p-*toluenesulphonyl* derivative separated from alcohol in stout prisms, m. p. 136—137° (Found : N, 4·7. $C_{17}H_{21}O_2NS$ requires N, 4·6%). It was soluble in methyl alcohol, ether, benzene, and ethyl acetate, not readily soluble in carbon tetrachloride, and sparingly soluble in light petroleum (b. p. 40—60°). It yielded a sodium salt which was only sparingly soluble in sodium hydroxide solution.

p-Amino*iso*butylbenzene, when warmed in light petroleum with a slight deficiency of phenylthiocarbimide, yielded p-iso*butyldiphenylthiocarbamide* as a sparingly soluble, crystalline powder, which separated from alcohol in silvery plates, m. p. 130—131° (Found : N, 9·9. $C_{17}H_{22}N_2S$ requires N, 9·9%). It was not readily soluble in cold alcohol, or in ether, but was more soluble in benzene or ethyl acetate.

p-Amino*iso*butylbenzene was converted through the diazo-compound into *iso*butylchlorobenzene, which was oxidised, by warming with an excess of chromic acid in presence of dilute sulphuric acid, to *p*-chlorobenzoic acid, m. p. and mixed m. p. 234°.

Rearrangement of iso*Butylaniline in Open Tubes or in a Current of Nitrogen.*—The experimental conditions were identical with those described previously (this vol., p. 1561; J., 1927, 64). The results are summarised in the following table :—

Wt. of amine, g.	Salt.	Duration, hrs.	Temp.	Yield of primary amine.	Exptl. conditions.
4·7	$ZnBr_2$	15½	210—240°	2·12	Stream of N_2
14·2	$CoCl_2$	15	220	10·3	,, ,,
4·7	$CoBr_2$	16	220—230	0·7*	,, ,,
7·6	CoI_2	15½	215	2·16*	,, ,,
9·5	$CdCl_2$	15	215—230	3·45	Open tube

* In these two experiments there was a loss of the secondary amine by volatilisation during the early part of the experiment. The loss was particularly severe in the experiment using cobalt bromide.

The separation of the primary amine from unchanged secondary amine was effected through its sparingly soluble zincichloride, and it was subsequently converted into its acetyl compound. The acetyl compound obtained in each experiment consisted almost entirely of *p*-acetamido*iso*butylbenzene, and crystallisation from alcohol yielded the pure compound, m. p. and mixed m. p. 127—128°.

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