XV.—*Intramolecular Rearrangement of the Alkyl-arylamines: Formation of* 4-*Amino-*n-*butylbenzene.*

By JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM.

AN important reaction of many of the N-substitution products of the arylamines is their rearrangement to C-substitution compounds. This change occurs with the majority of the common substituent groups, such as halogen, nitro-, nitroso-, sulphonyl, and alkyl. The intramolecular change of the chloroarylamines may be explained in terms of the variable valency of the nitrogen atom (compare Blanksma, *Rec. trav. chim.*, 1903, **22**, 290; Orton and Jones, *Rep. Brit. Assoc.*, 1910). The formation of p-chloroacetanilide from N-chloroacetanilide is accompanied by the formation of an additive compound (compare Armstrong, T., 1900, **77**, 1051). The presence of a catalyst is necessary in many molecular changes involving the migration of a nitroso- or nitro-group, as in the production of p-nitrosoalkylanilines from nitrosoamines and of nitroanilines from nitroamines. Whilst the bromo- and chloro-aniline derivatives have been thoroughly investigated, as well as the nitroso- and sulphonyl

substituted alkylanilines, the intramolecular change of the alkyl-arylamines has not been dealt with in such detail.

The earlier work in the production of aminoalkylbenzenes showed that they could be formed either by heating (*a*) aniline hydrochloride and the alcohol, or (*b*) the alkylaniline hydrochloride, at temperatures above 300° (compare Hofmann, *Ber.*, 1872, **5**, 729). Since methylaniline hydrochloride on heating in a current of hydrogen chloride yields methyl chloride, it has been generally assumed that a somewhat similar reaction would occur in an autoclave or sealed tube on heating the alkylaniline hydrochloride.

On heating *n*-butylaniline hydrochloride in a sealed tube, amino-*n*-butylbenzene was the main product. In addition, ammonia, aniline, and 4-butylamino-*n*-butylbenzene were formed, together with smaller amounts of more highly butylated products. There was also obtained a portion soluble in concentrated hydrochloric acid, and precipitated on dilution, which probably contained diphenylamine derivatives. In addition to the hydrochloride, the alkylaniline zincichloride and certain other compounds with metallic salts also undergo this transformation on heating. The chief product resulting from the intramolecular rearrangement of *n*-butylaniline is, however, 4-amino-*n*-butylbenzene. To explain the formation of this compound from *n*-butylaniline it might be supposed that the latter decomposes partly to aniline and *n*-butyl chloride or butylene; either of the last two might then be supposed to react with aniline. The production of *n*-butyl chloride is probably excluded in the case where zinc chloride replaces the hydrochloric acid. By heating *n*-butylaniline hydrochloride in a sealed tube or in an open flask, a small amount of a gas is obtained, which resembles butylene in being unsaturated. It appears possible that butylene may result as an intermediate product in the change. By heating *n*-butylaniline hydrochloride under atmospheric pressure a certain amount of 4-aminobutylbenzene is produced. If butylene is formed as an intermediate product, some *sec.*-butylbenzene should be obtained. An examination of the end-products shows that amino-*sec.*-butylbenzene is present, generally, at the most, only in traces.

The orientation of aminobutylbenzene (I), obtained by the intramolecular rearrangement of *n*-butylaniline, was determined by con-
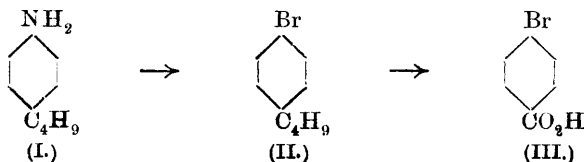

(I.)   (II.)   (III.)

verting the purified amino-derivative into bromobutylbenzene (II), which, on oxidation with chromic acid, gave *p*-bromobenzoic acid (III).

It cannot be assumed with certainty that *n*-butyl alcohol and aniline zincichloride will yield a compound containing a *n*-butyl group. An examination of the literature shows that a rearrangement of the alkyl group often occurs when it is introduced into the benzene ring. The rearrangement of the *n*-butyl chloride and *iso*butyl chloride in the formation of butylbenzenes by the Friedel and Crafts reaction is well established. The rearrangement of alkyl groups in the formation of aminoalkylbenzenes also appears to take place. Effront (*Ber.*, 1884, **17**, 2324), by the action of *iso*butyl alcohol on *o*-toluidine hydrochloride, obtained 5-*tert.*-butyl-*o*-toluidine, which by the diazo-reaction yielded a phenol identical with that obtained by heating *tert.*-butyl chloride, *o*-cresol, and zinc chloride (compare Baur, *Ber.*, 1894, **27**, 1615). It is also probable that by the action of *iso*butyl alcohol on aniline hydrochloride amino-*tert.*-butylbenzene is obtained. The recorded physical constants of the derivatives of 4-amino*iso*butylbenzene and 4-*amino-tert.*-butylbenzene are practically identical, and doubt must be thrown on their existence as two compounds (compare Studer, *Annalen*, 1882, **211**, 234; Senkowski, *Ber.*, 1890, **23**, 2412; Malherbe, *Ber.*, 1919, **52**, [*B*], 319).

It became necessary, therefore, to determine the configuration of the butyl group of the primary amine from *n*-butyl alcohol and aniline. By heating aniline zincichloride with *sec.*-butyl alcohol an amine was obtained, boiling at 240°, or 20° lower than that obtained from the normal alcohol, and yielding a different series of derivatives. As there was only a small quantity of this amine available it was not possible to determine the orientation of the butyl groups. Any doubt that the primary amine from *n*-butyl alcohol boiling at 258° was not a normal derivative was removed by preparing from it the other two monoamino-compounds. A comparison of the derivatives of the amines thus prepared shows that the amine from *sec.*-butyl alcohol differs from the one from *n*-butyl alcohol in the configuration of the butyl group.

By the nitration of 4-*acetylamino*-n-*butylbenzene*, followed by hydrolysis, 3-*nitro-4-amino*-n-*butylbenzene* (IV) was obtained as a red solid of low melting point. The orientation of the nitro-group was determined by converting the compound into a diamine, which condensed with benzil to yield 2:3-*diphenyl*-6-n-*butylquinoxaline* (XVIII). On eliminating the amino-group from 3-nitro-4-amino-butylbenzene, 3-*nitro*-n-*butylbenzene* (V) was obtained as a pale yellow oil boiling at 275—277°.
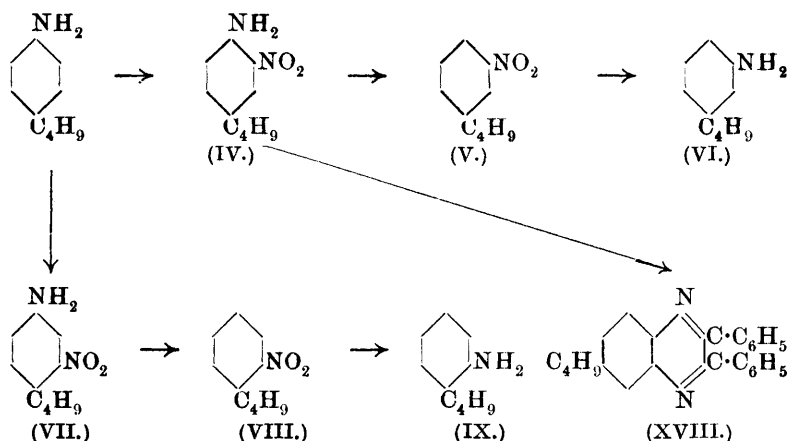
Nitration of 4-amino-*n*-butylbenzene in the presence of sulphuric acid gave 2-*nitro*-4-*amino*-n-*butylbenzene* (VII), melting at 52°, which by the diazo-reaction yielded 2-*nitro*-n-*butylbenzene* (VIII), a yellow oil distilling with some decomposition. Reduction of 2-nitro- and 3-nitro-*n*-butylbenzenes gave primary amines, the derivatives of which are distinct from those obtained from the primary amine boiling at 240° from *sec.*-butyl alcohol.   It must be concluded, therefore, that in the intramolecular transformation of *n*-butyl-aniline 4-amino-*n*-butylbenzene is obtained.

The following table shows clearly the difference between the amines obtained :

|	Acetyl compound, m. p.	Benzoyl compound, m. p.
2-Amino-*n*-butylbenzene	100°	—
3-Amino-*n*-butylbenzene	Not obtained crystalline.	68°
4-Amino-*n*-butylbenzene	105°	126°
4-Amino-*sec.*-butylbenzene ...	126°	—

Although *n*-butyl alcohol reacts with aniline zincichloride to yield 4-amino-*n*-butylbenzene, it gives with phenol, in the presence of zinc chloride, hydroxy-*sec.*-butylbenzene.   The constitution of the latter compound was shown by its identity with the hydroxy-derivative obtained from 4-amino-*sec.*-butylbenzene (XI) by the aid of the diazo-reaction.
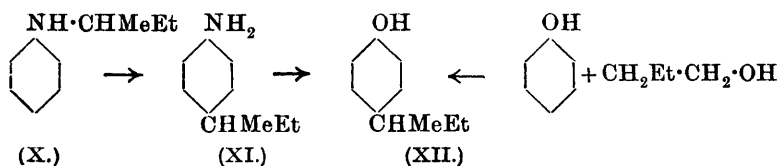
It has been shown by Mailhe and Godon (*Compt. rend.*, 1918, **166**, 467) that methylaniline and methyltoluidine are stable at moderately high temperatures, as they may be produced by passing a mixture of methyl alcohol and the primary arylamine over a suitable catalyst heated to 400°. No intramolecular rearrangement is observed when methyl- or ethyl-aniline is passed over heated nickel; instead, a decomposition into aniline and methane or ethylene occurs (Sabatier and Gaudion, *Compt. rend.*, 1917, **165**, 309). It has been found that n-butylaniline may be heated for several hours at 240—260° without the production of any amino-butylbenzene. Furthermore, the addition of substances which show no tendency to combine with butylaniline, such as calcium sulphate, sodium chloride, or silica, does not bring about any migration of the alkyl group to the nucleus. The formation of 4-amino-n-butylbenzene from n-butylaniline has been observed to take place only when a substance is added which combines with butylaniline. Substances such as hydrochloric acid, zinc chloride, cobalt chloride, and cadmium chloride have been chiefly employed, and with all these salts the additive compounds have been isolated. It appears that for intramolecular rearrangement of the alkylarylamines to occur, the presence of a substance which is capable of uniting with the amino-group is necessary.

The rearrangement of n-butylaniline cannot be satisfactorily explained by assuming the intermediate formation of either butyl chloride or butylene. Orton (*loc. cit.*) has suggested that amino-benzenes and their N-substituted derivatives are capable of existing as dynamic isomerides. It is possible that the transference of the alkyl group to the nucleus might occur during one of these phases. To attempt to explain the intramolecular rearrangement of alkyl-arylamines, the alkyl groups attached to the aminic nitrogen are assumed tentatively to exist in a state of oscillation, following a system of vibration which is definite as long as the external conditions remain constant. The calling into play of the residual valency of the nitrogen atom will have the effect of introducing more groups round the nitrogen atom, with the result that a rearrangement of the alkyl groups may occur. The disturbing effect will depend on several factors, such as the space occupied by each group, its vibration path, and also the polarity of the group. The groups already attached to the nitrogen will have the effect of hindering the entry of another group, corresponding with the space occupied by them. They will also tend to be displaced farther away from the nitrogen atom according to the hindrance produced by them, and there will be a tendency for the alkyl groups to be removed in the order of their steric relations to one another.

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Experiments were carried out in order to measure the relative ease with which differing alkyl groups were expelled from the alkyl-anilines. The earlier measurements were made by heating the monomethyl- and monobutyl-anilines separately in sealed tubes under similar conditions, so far as possible, with various substances. The results indicate that n-butylaniline undergoes intramolecular change the more readily, but the method is open to several objections. It was impossible to ensure absolutely identical conditions for each substance, such as the same temperature and pressure inside each tube. It is also likely that in the formation of the additive compounds of the alkylanilines, steric effects may have an influence, so that the rearrangement caused in the molecule may be counterbalanced to some extent by the steric hindrance due to the alkyl group. To overcome these probable sources of error the intramolecular rearrangement of dissimilarly substituted tertiary alkyl-anilines has been investigated. Methyl-n-butylaniline (XIII) was heated in a sealed tube in the presence of hydrogen chloride, zinc chloride, or cobalt chloride. The products of the rearrangement should then indicate whether the larger alkyl groups are the more readily removed. Thus methyl-n-butylaniline should yield as a first step methylaminobutylbenzene (XVI) or butyltoluidine (XIV), according to whether the butyl or the methyl group is the more mobile.
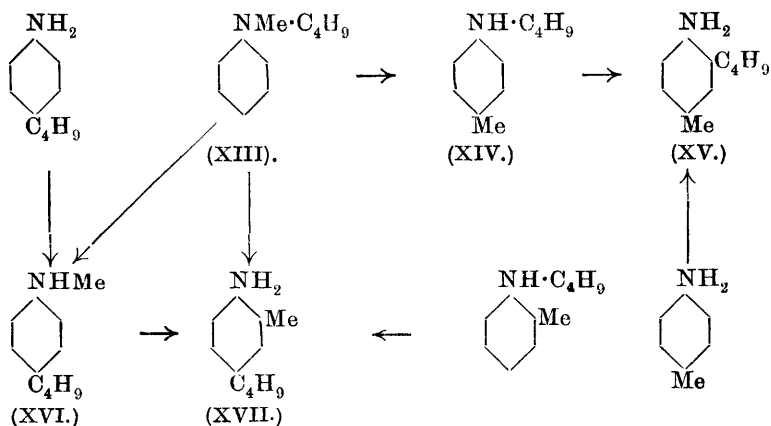
The constitution of the product was determined by dissolving the mixture of amines in dilute hydrochloric acid and adding in slight excess a solution of sodium nitrite. The secondary amines were removed as nitrosoamines, which could be converted into solid nitro-derivatives. Any diazonium salt in the solution was converted into the corresponding azo-β-naphthol derivative, which

would serve to identify the primary amine originally present. An examination of the products of nitration of the secondary amines resulting from the intramolecular rearrangement of methyl-*n*-butyl-aniline indicated that a mixture was present, from which 3 : 5-di-nitro-*n*-butyl-*p*-toluidine and 2 : 4 : 6-trinitrophenylmethylnitroamine were isolated in small quantities. It has not yet been possible to determine the complete composition of the mixture.

The *azo-β-naphthol* compounds were reduced, yielding the original primary amines present after intramolecular change had taken place. Analytical results showed that these amines were amino-methylbutylbenzenes, although in one case *p*-tolueneazo-β-naphthol was isolated in small amount by recrystallisation of the azo-β-naph-thols. It appears, therefore, that in the reaction both the methyl and butyl groups have undergone intramolecular rearrangement, and until a method has been elaborated for determining the composition of the products it is not possible to determine accurately the relative ease with which the different alkyl groups are removed.

The elimination of alkyl groups of alkylanilines on heating in a current of hydrogen chloride was also investigated. The secondary amines present in the mixture were isolated as nitrosoamines, and these were nitrated in glacial acetic acid by means of fuming nitric acid and converted into the corresponding trinitrophenylalkylnitro-amines. It was found that methyl-*n*-butylaniline yielded a mixture of secondary amines, and 2 : 4 : 6-trinitrophenylmethylnitroamine was isolated from the mixture of nitroamines. The melting point of the nitration product was lower than either that of trinitro-phenylmethylnitroamine or the corresponding butyl derivative, and was probably a mixture containing these two compounds.

In experiments on the elimination of alkyl groups from dissimi-larly substituted alkylarylamines it is essential to use a pure tertiary amine, unmixed with any secondary amine. The methyl-*n*-butyl-aniline employed was purified by fractionation, followed by heating it with phenylcarbimide. The boiling point of the amine obtained in this way differed considerably from that recorded by Komatsu (*Mem. Coll. Sci. and Eng. Kyoto Imp. Univ.*, 1912, **3**, 371), who also prepared this amine. He records the boiling point as 225—230°, and states that it yields a picrate melting at 143°. Methyl-*n*-butyl-aniline, purified in the manner indicated above, boils at 242·5° and yields a picrate melting at 90°. The melting point of the picrate is thus brought into agreement with those of other tertiary butyl-anilines.

By increasing the size of the alkyl group in alkylbutylanilines the melting point of the picrate is raised. The following table shows

the effect of displacing the methyl group in methylbutylaniline by larger groups.

Methyl-*n*-butylaniline boils at 242·5°.   The picrate melts at   90°.
Ethyl-*n*-butylaniline   ,,   248°.   ,,   ,,   ,,   100°.
Di-*n*-butylaniline   ,,   260—263°.   ,,   ,,   ,,   125°.

The nitration of tertiary alkylanilines was also studied.   On nitrating methylbutylaniline under vigorous conditions, the principal product is 2 : 4 : 6-trinitrophenylmethylnitroamine, showing that the larger group has been eliminated.   Meldola and Hollely (T., 1915, **107**, 610) have found that in the nitration of acetylated *as*-dialkylphenylenediamines a similar action occurs, the larger groups being removed in the nitration, in preference to the smaller groups.

On nitrating ethyl-*n*-butylaniline both trinitrophenylethylnitroamine and trinitrophenyl-*n*-butylnitroamine are produced.   The difference in the relative proportions of the two products of the nitration appears to be less than in the case of methyl-*n*-butylaniline.

Trinitrophenylmethylnitroamine is also obtained on nitrating dimethylaniline under vigorous conditions.   Toward the end of the operation there is the usual vigorous effervescence due to the elimination of the methyl group as carbon dioxide.   In nitrating di-*n*-butylaniline under similar conditions there is practically no effervescence, and from the mixture after nitration a volatile fatty acid was isolated, which was identified as *n*-butyric acid by means of its distillation constant.

EXPERIMENTAL.

The   Amino-derivative   of   n-*Butylbenzene :*   4-*Amino-*n-*butylbenzene.*

In the preparation of 4-amino-*n*-butylbenzene, *n*-butyl alcohol was allowed to react with aniline in the presence of a suitable condensing agent, such as zinc chloride.   Approximately molecular quantities of aniline and dry *n*-butyl alcohol were mixed with fused zinc chloride (0·5 mol.), and the mixture was heated in an electrically wound autoclave for twenty-four hours at 230—240°.   The product was washed first with water to remove uncombined zinc chloride and finally with ether or light petroleum (b. p. 80—100°).   In this way secondary amines and other by-products were removed, leaving behind the zincichlorides of the primary amines, from which a mixture of these amino-compounds was obtained by treatment with warm concentrated sodium hydroxide solution.   Fractionation of the mixture of bases yielded 4-amino-*n*-butylbenzene.   By using

amounts of zinc chloride less than the molecular proportion—even as low as one-seventh of the amount quoted above—4-amino-n-butyl-benzene was still produced, but the yield was not so good.

The *hydrochloride* is precipitated on adding an excess of concentrated hydrochloric acid to an aqueous suspension of the base. It is readily soluble in water or alcohol, but only sparingly so in an excess of hydrochloric acid :

0·1063 gave 6·9 c.c. N_2 at 21° and 751 mm. $N = 7\cdot5$.*
0·1420 ,, 0·1093 AgCl. $Cl = 19\cdot0$.

$\quad C_{10}H_{15}N,HCl$ requires $N = 7\cdot5$; $Cl = 19\cdot1$ per cent.

The *hydrobromide* crystallises from aqueous solution containing free hydrobromic acid in large, white plates. It is readily soluble in water or alcohol :

0·0785 gave 0·0654 AgBr. $Br = 34\cdot6$.

$\quad C_{10}H_{15}N,HBr$ requires $Br = 34\cdot7$ per cent.

The *sulphate* crystallises from moist ether in a felted mass of white crystals. It is sparingly soluble in water :

0·1002 gave 6·1 c.c. N_2 at 20° and 737 mm. $N = 6\cdot9$.
0·3502 ,, 0·2058 $BaSO_4$. $H_2SO_4 = 24\cdot7$.

$\quad (C_{10}H_{15}N)_2,H_2SO_4$ requires $N = 7\cdot1$; $H_2SO_4 = 24\cdot7$ per cent.

From warm alcohol it separated as a mass of colourless crystals which under the microscope had the appearance of interlaced laths.

The *platinichloride* is a pale brownish-yellow powder, sparingly soluble in water, and more readily so in alcohol. It crystallises from absolute methyl alcohol in small needles melting and decomposing at 200—202° :

0·1203 gave 0·0330 Pt. $Pt = 27\cdot4$.

$\quad (C_{10}H_{15}N)_2,H_2PtCl_6$ requires $Pt = 27\cdot6$ per cent.

The *acetyl* derivative, obtained from 4-amino-n-butylbenzene by the action of acetic anhydride, crystallises from alcohol in white plates melting at 105° :

0·1426 gave 8·8 c.c. N_2 at 17° and 755 mm. $N = 7\cdot3$.

$\quad C_{12}H_{17}ON$ requires $N = 7\cdot3$ per cent.

The *benzoyl* derivative, obtained by the Schotten-Baumann reaction, crystallises from alcohol in bulky groups of fine needles melting at 126° :

0·1015 gave 4·65 c.c. N_2 at 17° and 748 mm. $N = 5\cdot3$.

$\quad C_{17}H_{19}ON$ requires $N = 5\cdot5$ per cent.

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* In the nitrogen estimations recorded in this paper, the gas was measured over 40 per cent. potassium hydroxide solution, and the pressure has been corrected for vapour tension.

α-*Phenyl*-β-4-n-*butylphenylcarbamide*, $C_4H_9 \cdot C_6H_4 \cdot NH \cdot CO \cdot NHPh$.

4-Amino-n-butylbenzene was treated with a solution of one molecular proportion of phenylcarbimide dissolved in light petroleum (b. p. 60—80°), and after remaining at the ordinary temperature for two or three hours the precipitate was collected, washed several times with small quantities of light petroleum, and dried :

0·1002 gave 0·2790 CO_2 and 0·0678 H_2O.   C = 75·9 ; H = 7·5.

0·1012   ,,   9·1 c.c. N_2 at 20° and 757 mm.   N = 10·5.

$C_{17}H_{20}ON_2$ requires C = 76·1 ; H = 7·5 ; N = 10·4 per cent.

It crystallises from aqueous alcohol in bulky masses of small, white needles melting at 160°.   It is soluble in ether, acetone, ethyl acetate, or glacial acetic acid, but sparingly so in water or light petroleum.

4-*Bromo*-n-*butylbenzene*.

The orientation of the butyl group was determined by converting the amino-n-butylbenzene into a derivative that could yield a substituted benzoic acid by oxidation.   For this purpose the aminogroup was displaced by bromine by the Sandmeyer reaction. 4-Amino-n-butylbenzene was dissolved in three molecular proportions of hydrobromic acid and diazotised by the addition of sodium nitrite solution.   On adding a solution of cuprous bromide in hydrobromic acid, followed by distillation in a current of steam, 4-*bromo*-n-*butylbenzene* was obtained as a pale yellow oil of pleasant, ethereal odour, denser than water, and boiling at 242—243°/755 mm. :

0·0853 gave 0·1762 CO_2 and 0·0460 H_2O.   C = 56·4 ; H = 6·0.

$C_{10}H_{13}Br$ requires C = 56·3 ; H = 6·1 per cent.

That the bromo- and alkyl groups are in the para-position follows from the production of p-bromobenzoic acid by oxidation.   Half a gram was heated in a sealed tube with 12 c.c. of a 6 per cent. solution of chromic acid for seven hours at 150—200°.   There was practically no pressure on opening the tube, which contained a green, amorphous mass together with tarry matter and some white, glistening, needle-shaped crystals.   The contents of the tube were rendered alkaline, and after removing the suspended matter, a grey solid was precipitated on adding dilute sulphuric acid.   It was purified by dissolving in sodium carbonate solution, and any traces of volatile bromo-compounds were removed by means of a current of steam.   The addition of dilute hydrochloric acid precipitated a white solid which crystallised from ether in small needles melting at 250°.   This melting point is almost identical with that recorded for p-bromobenzoic acid (251°), and is considerably higher than those of the other two monobromobenzoic acids.

Diazoamino-4-n-butylbenzene.

The base (1 mol.) was dissolved in glacial acetic acid (3 mols.) and the solution diluted. On adding sodium nitrite solution, a yellow, semi-solid mass separated which quickly became hard. The diazoamino-4-n-*butylbenzene* was collected and, after washing several times with water to remove any traces of nitrous acid, crystallised from light petroleum, from which it separated in masses of slender, sulphur-yellow needles melting at 75°:

0·0743 gave 9·0 c.c. N_2 at 24° and 742·5 mm. $N = 13·7$.

$C_{20}H_{27}N_3$ requires $N = 13·6$ per cent.

When exposed to the light it darkened slowly.

4-n-*Butylbenzeneazo-β-naphthol*.

A solution of the hydrochloride of the base was diazotised and, after removing the excess of nitrous acid by means of carbamide, it was poured into an alkaline solution of β-naphthol. The red *azo*-compound crystallised from hot alcohol in bright red bunches of slender needles melting at 80°:

0·1088 gave 9·8 c.c. N_2 at 15·3° and 741 mm. $N = 9·4$.

$C_{20}H_{20}ON_2$ requires $N = 9·2$ per cent.

4-n-*Butylbenzeneazo-β-naphthol* is insoluble in a 30 per cent. solution of potassium hydroxide. It dissolves in concentrated sulphuric acid with the production of a brilliant purple colour, which gives place to a faint brown coloration on dilution.

4-n-*Butylbenzeneazophenyl-β-naphthylamine*.

This derivative was prepared by adding a diazotised solution of 4-amino-*n*-butylbenzene, freed from excess of nitrous acid, to one molecular proportion of phenyl-β-naphthylamine dissolved in acetic acid. An excess of sodium acetate was then added, and the red product was allowed to remain at the ordinary temperature for two to three hours, with occasional stirring. Water was added to complete the precipitation of the azo-compound, which was collected and purified after being washed with warm water:

0·1080 gave 10·2 c.c. N_2 at 17° and 750 mm. $N = 11·1$.

$C_{26}H_{25}N_3$ requires $N = 11·1$ per cent.

It is readily soluble in chloroform, benzene, or ether. In the presence of a small amount of ether the azo-compound dissolves in concentrated hydrochloric acid to yield an intense purplish-blue solution. After some time the colour disappears with the production of a dark precipitate which becomes red after keeping for a

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further period.   Concentrated sulphuric acid dissolves it with the production of an intense dark blue coloration, becoming red on dilution.

4-n-*Butylbenzeneazobenzoylacetone.*

A diazotised solution of 4-amino-*n*-butylbenzene (1 mol.), freed from nitrous acid by means of carbamide, was added to an alcoholic solution of benzoylacetone (1 mol.).   The addition of sodium acetate produced a bright yellow turbidity, from which a dark-coloured oil separated.   On keeping overnight in the ice-chest the oil solidified to a mass of dark yellow crystals which were collected, dried on a porous plate, and recrystallised.   The compound separated from ether in stellate groups of yellow crystals melting at 97—100° :

0·1588 gave 12·2 c.c. N_2 at 18° and 747 mm. $N = 8·9$.

$C_{20}H_{22}O_2N_2$ requires $N = 8·7$ per cent.

The substance is soluble in alcohol or ether, and dissolves in sulphuric acid with the production of a brown colour, giving place to a yellow opalescence on dilution.   Sulphuric acid containing a small amount of dissolved chromic acid also produces a similar coloration.

4-n-*Butylbenzeneazo*-2 : 7-*dihydroxynaphthalene.*

This compound was obtained as a dark red powder on adding a solution of the diazotised amine to an alcoholic solution of 2 : 7-dihydroxynaphthalene in the presence of an excess of sodium acetate. It was purified by washing with a dilute aqueous solution of sodium hydroxide, followed by extraction with chloroform.   It crystallised from hot glacial acetic acid in small, bronze-coloured crystals melting at 200—201° :

0·1588 gave 12·2 c.c. N_2 at 18° and 747 mm. $N = 8·9$.

$C_{20}H_{20}O_2N_2$ requires $N = 8·7$ per cent.

4-*Hydroxy*-n-*butylbenzene.*

4-Amino-*n*-butylbenzene (9 grams) was added to an aqueous solution containing sulphuric acid in excess (five molecular proportions), and, after cooling, diazotised by the addition of sodium nitrite. The mixture was stirred continuously, when the suspended sulphate gradually passed into solution.   The solution was filtered to remove any unchanged sulphate, treated with a large excess of concentrated sulphuric acid, and subsequently distilled in a current of steam. 4-*Hydroxy*-n-*butylbenzene* passed over as a pale yellow oil, and was

obtained pure by distillation. It is an almost colourless oil, possessing a faint phenolic odour, and boiling at 248°/765 mm.:

0·0818 gave 0·2387 CO_2 and 0·0686 H_2O. C = 79·6; H = 9·3.
$C_{10}H_{14}O$ requires C = 79·95; H = 9·4 per cent.

4-n-*Butylphenyl Phenylcarbamate*, $C_4H_9 \cdot C_6H_4 \cdot O \cdot CO \cdot NHPh$.

4-Hydroxy-*n*-butylbenzene was heated on the water-bath with slightly more than one molecular proportion of phenylcarbimide. On cooling, the solid mass was passed on a porous tile and crystallised from alcohol, from which it separated in white needles melting at 115°:

0·1059 gave 4·7 c.c. N_2 at 20° and 744 mm. N = 5·0.
$C_{17}H_{19}O_2N$ requires N = 5·2 per cent.

2-*Nitro*-4-*amino*-n-*butylbenzene*.*

4-Amino-*n*-butylbenzene was dissolved in two hundred times its weight of concentrated sulphuric acid and, after cooling to −5°, the calculated amount of nitric acid (1 mol.), dissolved in three times its weight of sulphuric acid, was added gradually. During the addition of the acid the mixture was continually stirred, and the temperature not allowed to rise above 5°. After eighteen hours the mixture was poured into ice-water, when a sparingly soluble sulphate was precipitated, which was collected and decomposed by the addition of aqueous ammonia. In this way a brown, crystalline solid was obtained consisting of 2-*nitro-4-amino*-n-*butylbenzene*. A further quantity was isolated by treating the acid filtrate with aqueous ammonia and extracting the solution with ether. It was obtained pure by dissolving it in aqueous methyl alcohol, and precipitating with water, followed by recrystallisation from warm light petroleum (b. p. 80—100°). It forms golden-yellow scales, readily soluble in ether and melting at 52°:

0·0739 gave 9·3 c.c. N_2 at 17·5° and 735 mm. N = 14·5.
$C_{10}H_{14}O_2N_2$ requires N = 14·4 per cent.

No evidence was obtained of the existence of the other isomeride.
The *hydrochloride* was obtained as a white precipitate by adding hydrochloric acid to an ethereal solution of the base and evaporat-

* The nitration of *n*-butyl-*p*-toluidine has been previously described as yielding 2-nitro-*n*-butyl-*p*-toluidine as a red oil (T., 1918, **113**, 988). On keeping over the winter it solidified to a mass of bright red crystals melting at 18—19°. By converting the substance into its hydrochloride, crystallising from alcohol, and decomposing with aqueous ammonia, 2-nitro-*n*-butyl-*p*-toluidine was obtained in large, rectangular, red plates which melted at 19°.

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ing the ether.   It crystallises from warm absolute methyl alcohol in masses of slender, colourless needles.   On heating, the colour changes to yellow.   A specimen melted at 190—195° after immersion in the bath at 150°, a rapid darkening in colour taking place at 185—190°:

0·1017 gave 0·0638 AgCl.   Cl = 15·5.

$C_{10}H_{14}O_2N_2,HCl$ requires Cl = 15·4 per cent.

The *sulphate* is sparingly soluble in dilute sulphuric acid.   It crystallises from warm alcohol containing some sulphuric acid in small, white plates which are hydrolysed by water:

0·0811 gave 6·35 c.c. N_2 at 13·2° and 761 mm.   N = 9·4.

$C_{12}H_{16}O_3N_2,H_2SO_4$ requires N = 9·6 per cent.

2-*Nitro*-n-*butylbenzene.*

2-Nitro-4-aminobutylbenzene (2·5 grams) was diazotised in aqueous alcoholic solution in the presence of sulphuric acid, a small amount of insoluble matter was removed, and the diazo-group was eliminated by heating with an excess of alcohol, when 2-*nitro*-n-*butylbenzene* was obtained.   It is a pale yellow oil possessing a characteristically pleasant odour.   It is readily volatile in steam, and apparently so in alcohol vapour, for on removing the alcohol by distillation after eliminating the diazo-group, appreciable amounts of the nitro-compound were obtained in the alcoholic distillate.

It distils with some decomposition at about 260° under the ordinary pressure :

0·0814 gave 5·4 c.c. N_2 at 20° and 746 mm.   N = 7·6.

$C_{10}H_{13}O_2N$ requires N = 7·8 per cent.

2-*Amino*-n-*butylbenzene.*

Reduction of the nitro-compound was effected by means of zinc dust or tin foil and hydrochloric acid.   The amine was isolated by extraction with ether after rendering the acid liquid alkaline. 2-*Amino*-n-*butylbenzene* is a yellow oil, possessing a rather unpleasant odour recalling that of aniline :

0·0746 gave 5·9 c.c. N_2 at 16° and 750 mm.   N = 9·3.

$C_{10}H_{15}N$ requires N = 9·4 per cent.

The *acetyl* derivative crystallises from warm aqueous methyl alcohol in masses of small, white needles melting at 100°:

0·0819 gave 5·5 c.c. N_2 at 20·5° and 749 mm.   N = 7·7.

$C_{12}H_{17}ON$ requires N = 7·3 per cent.

The melting point of this compound is very close to that of

4-acetylamino-n-butylbenzene.   It was shown to be distinct from
that substance, for a mixture of these acetyl derivatives commenced
to melt at 75° and had completely melted at 85°.

3-$Nitro$-4-$amino$-n-$butylbenzene$.

The most convenient method of obtaining this compound in a
pure state was to nitrate 4-acetylamino-n-butylbenzene by means of
fuming nitric acid, afterwards eliminating the acetyl group.

3-$Nitro$-4-$acetylamino$ - n - $butylbenzene$.—The acetyl compound
(2 grams) was dissolved in 20 c.c. of glacial acetic acid, the solution
cooled to $-5°$, and 15 grams of nitric acid (D 1·5) were added
slowly, so that the temperature did not rise above 5°.   After an
hour the mixture was poured into ice-water, and the yellow precipi-
tate collected. The nitro-compound is soluble in most of the common
organic solvents except light petroleum, and crystallises very readily
from hot alcohol in slender, canary-yellow needles melting at 76°:

0·0649 gave 6·8 c.c. N_2 at 20° and 746·6 mm. $N = 12·0$.

$C_{12}H_{16}O_3N_2$ requires $N = 11·9$ per cent.

$Titration$ $with$ $Titanous$ $Chloride$.—0·01522 required 16·6 c.c.
$TiCl_3$ (1 c.c. $= 0·001297$ gram Fe).   Calc. as $C_{12}H_{16}O_3N_2 = 100·4$ per
cent.

On triturating it in a mortar with a 50 per cent. solution of
potassium hydroxide the colour changed from pale yellow to deep
brown.   After remaining for some time there was still a considerable
amount of the unchanged acetyl derivative together with some
3-$nitro$-4-$amino$-n-$butylbenzene$.   The latter compound was obtained
more conveniently by hydrolysis with alcoholic hydrogen chloride.
To the nitroacetyl compound dissolved in ten times its weight of
alcohol, an amount of hydrochloric acid, insufficient to precipitate
the nitro-compound, was added, and the mixture was heated under
reflux until, on pouring into dilute hydrochloric acid, no precipitate
was obtained.   On evaporation, 3-nitro-4-amino-n-butylbenzene was
left as a reddish-brown oil, which solidified in the ice-chest to a mass
of reddish-yellow needles melting at about 13°.   The substance was
purified by converting it into the hydrochloride, and decomposing
this with water or dilute ammonia:

0·0880 gave 11·0 c.c. N_2 at 18·5° and 745 mm. $N = 14·4$.

$C_{10}H_{14}O_2N_2$ requires $N = 14·4$ per cent.

$Titration$ $with$ $Titanous$ $Chloride$.—0·01038 required 13·3 c.c.
$TiCl_3$ (1 c.c. $= 0·001344$ gram Fe).   Calc. as $C_{10}H_{14}O_2N_2 = 100·8$ per
cent.

The $hydrochloride$ crystallises from a mixture of alcohol and ether
in flat, shining plates.   It is readily hydrolysed by water.

Reduction of the base by adding zinc dust to a warm solution in hydrochloric acid gave 4-n-*butyl*-o-*phenylenediamine* as a viscous oil which is very readily oxidised on exposure to the air. On this account it was not isolated in a pure state for analysis, and the condensation product with benzil was prepared from its solution.

3-Nitro-4-amino-n-butylbenzene (1·4 grams) was dissolved in an excess of 50 per cent. aqueous acetic acid, and after raising the solution to the boiling point small quantities of zinc dust were added until the reduction was complete. Benzil (1·5 grams), dissolved in warm sodium hydrogen sulphite solution, was added and the mixture boiled for five minutes. A reddish-brown oil was produced, which on cooling settled to the bottom of the flask as a semi-solid mass. It was collected and, after pressing on a porous tile, crystallised from hot methyl alcohol. Pale yellow, flocculent masses of small crystals were obtained on rapid cooling and small, pale yellow needles, melting at 82°, by slow cooling. By spontaneous evaporation of an ethereal solution, large, well-defined groups of needle-shaped crystals separated :

0·0988 gave 6·8 c.c. N_2 at 15·0° and 768 mm. $N = 8·3$.
$C_{24}H_{22}N_2$ requires $N = 8·3$ per cent.

2 : 3-*Diphenyl*-6-n-*butylquinoxaline* (XVIII) is readily soluble in chloroform. It dissolves in cold, concentrated sulphuric acid with the production of an orange colour, which on dilution gives place to a white turbidity. It is also soluble in a large excess of concentrated hydrochloric acid, giving a yellow solution.

3-*Nitro*-n-*butylbenzene*.

3-Nitro-4-amino-n-butylbenzene was dissolved in hydrochloric acid (2·5 mols.) mixed with an equal volume of alcohol, and the solution cooled to −5°. A slight excess of sodium nitrite solution was added, and after about an hour some red, resinous matter was filtered off and the filtrate heated with an excess of ethyl alcohol under reflux for two hours. The alcohol was evaporated on the water-bath, and the volatile nitro-compound removed from the residue by distillation in a current of steam. 3-*Nitro*-n-*butylbenzene* was obtained as a yellow liquid having a pleasant odour :

0·0766 gave 5·4 c.c. N_2 at 20° and 747 mm. $N = 8·1$.
$C_{10}H_{13}O_2N$ requires $N = 7·8$ per cent.

The compound distils at 275°/752 mm. with no appreciable decomposition. It is apparently volatile to some extent in alcohol vapour, for on removing the excess of alcohol from the product of the diazo-reaction some of it was obtained in the distillate. It is

REARRANGEMENT OF THE ALKYLARYLAMINES. 119

miscible with chloroform, nitrobenzene, pyridine, or light petroleum.

3-*Amino*-n-*butylbenzene*.

To the nitro-compound suspended in concentrated hydrochloric acid, small pieces of tin foil were added from time to time until the reduction was complete. The tin in solution was removed as sulphide, and after rendering the liquid alkaline with sodium hydroxide solution, the amine was removed by extraction with ether. It was further purified by distillation in a current of steam.

3-*Amino*-n-*butylbenzene* is a pale yellow oil, lighter than water, and possesses a faint, agreeable odour:

0·1454 gave 12·5 c.c. N_2 at 25° and 727 mm.   N = 9·6.

$C_{10}H_{15}N$ requires N = 9·4 per cent.

The addition of an excess of warm concentrated hydrochloric acid yielded the *hydrochloride* as an oil which solidified on cooling to an interlaced mass of small, flattened, jagged needles.

The *acetyl* compound was obtained as an oil, which slowly hardened to a vitreous mass on keeping it in a desiccator:

0·0744 gave 4·9 c.c. N_2 at 25° and 745 mm.   N = 7·4.

$C_{12}H_{17}ON$ requires N = 7·3 per cent.

The *benzoyl* derivative, prepared by the Schotten-Baumann reaction, separates from alcohol in small, white, needle-shaped crystals, which melt at 68°:

0·1610 gave 7·8 c.c. N_2 at 17° and 748 mm.   N = 5·7.

$C_{17}H_{19}ON$ requires N = 5·5 per cent.

4-*Amino*-sec.-*butylbenzene*.

To show that no intramolecular rearrangement of the butyl group had occurred when *n*-butyl alcohol and aniline zincichloride interacted, the corresponding amine was prepared from *sec.*-butyl alcohol, which was obtained from *n*-butyl alcohol through the intermediate formation of butylene. In the presence of sulphuric acid, butylene yielded *sec.*-butyl alcohol, which was obtained pure by repeated fractionation. It boiled at 99·6—99·9°.

Aniline zincichloride was heated with one molecular proportion of *sec.*-butyl alcohol in an autoclave at 180° for sixty hours, the product being treated in exactly the same way as described above when *n*-butyl alcohol was used. The mixture of primary amines from the zincichloride was fractionated, and yielded, among other distillates, a fraction boiling between 230° and 250°. On redistilling this portion several times a primary amine was obtained boiling at 238°/762 mm. From the mixture of secondary amines soluble

in light petroleum, a primary amine was isolated by means of its sulphate, boiling at 238° and identical with the amine obtained from the mixture of primary bases:

0·1909 gave 16·0 c.c. N_2 at 19·5° and 740 mm. $N = 9·6$.

$C_{10}H_{15}N$ requires $N = 9·4$ per cent.

4-*Amino*-sec.-*butylbenzene*, on keeping, slowly changes in colour from very pale yellow to dark red. The diazonium salt gives a red *azo*-compound with β-naphthol in alkaline solution. With bleaching powder solution the amine gave no coloration. The addition of a solution of chromic acid in concentrated sulphuric acid produced a dirty green coloration, changing through purple to wine-red on dilution. Nitric acid added in small amount to the sulphate of the amine suspended in concentrated sulphuric acid coloured the solid matter purple, and the solution yellowish-brown.

The *hydrochloride* is precipitated from aqueous solution on the addition of an excess of hydrochloric acid:

0·0987 gave 0·0750 AgCl. Cl = 18·8.

$C_{10}H_{15}N,HCl$ requires Cl = 19·1 per cent.

The *sulphate* is sparingly soluble in cold water, but more readily so in hot water, from which it separates in masses of white crystals.

The *acetyl* derivative crystallises from aqueous alcohol in lustrous, white plates melting at 125—126°:

0·1540 gave 10·0 c.c. N_2 at 19° and 744 mm. $N = 7·5$.

$C_{12}H_{17}ON$ requires $N = 7·3$ per cent.

It is soluble in acetone, ether, or ethyl acetate, and sparingly so in water. No coloration is obtained by the addition of a solution of chromic acid in concentrated sulphuric acid.

With fuming nitric acid in glacial acetic acid solution it yields a yellow, crystalline *nitro*-derivative.

α-*Phenyl*-β-4-sec.-*butylphenylcarbamide*,
$CHMeEt·C_6H_4·NH·CO·NHPh$.
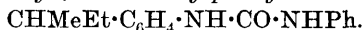
This derivative is prepared by the addition of phenylcarbimide to 4-amino-*sec.*-butylbenzene. It crystallises from aqueous alcohol in silky needles melting at 144°:

0·0730 gave 6·5 c.c. N_2 at 14° and 756 mm. $N = 10·6$.

$C_{17}H_{20}ON_2$ requires $N = 10·4$ per cent.

It is soluble in ether, acetone, or toluene, but only sparingly so in light petroleum (b. p. 60—80°).

In addition to amino-*sec.*-butylbenzene, other amines were obtained from the product of the action of heat on the mixture of *sec.*-butyl alcohol and aniline zincichloride. At 270—280° a fraction

was obtained consisting mainly of a primary amine, which on further purification boiled mainly between $274°$ and $278°$. This consisted apparently of aminodi-*sec.*-butylbenzene. A small quantity of a residue of a still higher boiling point was obtained, but it was not further investigated. The fractions of lower boiling points contained a considerable amount of a secondary amine, which was freed from the greater part of the primary amine by treatment with dilute sulphuric acid. In this manner a fraction was obtained boiling at 225—$235°$ consisting chiefly of *sec.*-butylaniline, which was obtained in a pure state by the action of *sec.*-butyl chloride on aniline. Aniline (1 mol.) was heated under a reflux condenser with *sec.*-butyl chloride ($1·5$ mols.); this contained a small amount of dissolved iodine, and was added gradually over a period extending over twenty-four hours. The purplish-blue product was rendered alkaline, and from the ethereal extract the sec.-*butylaniline* was precipitated as the zincichloride, the base being purified by distillation. It distilled at 224—$225°/765$ mm. as an almost colourless oil which had a pleasant, floral odour distinct from that of the corresponding *n*-butyl derivative:

$0·0928$ gave $0·2732$ CO_2 and $0·0866$ H_2O. $C = 80·3$; $H = 10·4$.

$0·0835$,, $6·7$ c.c. N_2 at $14°$ and 756 mm. $N = 9·5$.

$C_{10}H_{15}N$ requires $C = 80·5$; $H = 10·1$; $N = 9·4$ per cent.

It is miscible with most of the common organic solvents. The addition of a solution of chromic acid in concentrated sulphuric acid led to the production of no characteristic coloration. On adding a small quantity of nitric acid to a solution of the amine in concentrated sulphuric acid a reddish-brown coloration was observed.

The *hydrochloride* was obtained as a hard, crystalline mass by saturating a benzene solution of *sec.*-butylaniline with dry hydrogen chloride:

$0·1324$ gave $0·1030$ AgCl. $Cl = 19·2$.

$C_{10}H_{15}N,HCl$ requires $Cl = 19·1$ per cent.

It crystallises from warm benzene in hard nodules, which in bulk are grey. It is very readily soluble in water.

By the action of nitrous acid on the solution of the hydrochloride *phenyl*-sec.-*butylnitrosoamine* was obtained as a pale yellow oil, possessing an agreeable odour. It is volatile in steam:

$0·0924$ gave $12·6$ c.c. N_2 at $18·7°$ and 753 mm. $N = 15·9$.

$C_{10}H_{14}ON_2$ requires $N = 15·7$ per cent.

p-sec.-*Butylphenol*.

On diazotising amino-*sec.*-butylaniline sulphate and boiling the solution, nitrogen was evolved, and the liquid assumed a reddish-

brown colour due to the production of *p-sec.*-butylphenol. It was purified by distillation in a current of steam, followed by fractionation.

At 238° *p-sec.*-butylphenol passed over as a pale oil, solidifying to a mass of long, hair-like, white needles, melting at 59°. The melting point was not altered after two crystallisations from light petroleum. (Estreicher, *Ber.*, 1900, **33**, 436, gives m. p. 53—54°, b. p. 239·5—240·5°/750·6 mm.) The substance is very readily soluble in alcohol or ether, and, when treated with a dilute solution of chromic acid in concentrated sulphuric acid, gives no characteristic coloration, other than the production of a transient red tint. Ferric chloride also gives no coloration. (Found: $C = 79·9$; $H = 9·9$. $C_{10}H_{14}O$ requires $C = 79·95$; $H = 9·4$ per cent.) It is miscible with most of the common organic solvents. This compound was also obtained, probably in an impure state, by the action of *n*-butyl alcohol on phenol. In this reaction a rearrangement of the alkyl group occurs.

The boiling point of the phenol agrees with that of the substance prepared by the diazo-reaction. It was not, however, obtained crystalline, nor were any crystalline derivatives prepared from it. It seems probable that *p-sec.*-butylphenol is not the only product of the interaction between *n*-butyl alcohol and phenol in the presence of zinc chloride.

Phenol (100 grams) was heated with fused zinc chloride (240 grams) and *n*-butyl alcohol (80 grams) for twelve hours. On cooling, the mixture had separated into two layers. The addition of water dissolved the lower layer consisting mainly of zinc chloride, whilst the dark-coloured oil was removed. It consisted chiefly of *p-sec.*-butylphenol, together with some ethers which were removed by dissolving the phenol in sodium hydroxide solution. On distillation the main fraction was collected between 235° and 245° as a colourless oil of agreeable odour. Further fractionation gave a colourless, viscous oil distilling at 237—240°.

On the addition of a diazotised solution of β-naphthylamine to a solution of the phenol in dilute potassium hydroxide solution, a brown liquid was obtained, from which a reddish-brown *azo*-compound was isolated on rendering acid and extracting with solvents. It was not, however, obtained in a pure state.

The acetyl derivative, prepared by heating 5 grams of *p-sec.*-butylphenol with an excess of fused sodium acetate and 10 grams of acetic anhydride for three hours, was obtained as a colourless oil boiling at 244—246°/760 mm. (Estreicher, *loc. cit.*, gives 255·5°/743·9 mm.).

The *benzoyl* derivative, obtained by the Schotten-Baumann method, is an almost colourless, viscous oil:

0·0686 gave 0·2023 CO_2 and 0·0430 H_2O.   C = 80·4; H = 7·0.
$C_{17}H_{18}O_2$ requires C = 80·3; H = 7·1 per cent.

By nitrating crude *p-sec.*-butylphenol with concentrated nitric acid, mixtures of mono- and dinitro-derivatives were obtained. A better yield of the former was obtained by using dilute nitric acid.

p-sec.-Butylphenol (2·5 grams) was added to nitric acid (6 grams : D 1·5) and water (9 grams), the mixture being cooled in a stream of cold water. After sixteen hours the supernatant layer of acid was poured off and the residual oil distilled in a current of steam.

Nitro-p-sec.-*butylphenol* was obtained in this way as a red oil, which was purified by distillation under diminished pressure, when it distilled at 196—200°/80 mm.:

0·1452 gave 9·0 c.c. N_2 at 16° and 741 mm.   N = 7·2.
$C_{10}H_{13}O_3N$ requires N = 7·2 per cent.

The addition of aqueous ammonia precipitated the *ammonium* salt, and solutions of sodium and potassium hydroxides precipitated the corresponding alkali salts.

Reaction with Phenylcarbimide.

By heating *p-sec.*-butylphenol, prepared from *n*-butyl alcohol, at 100° with one molecular proportion of phenylcarbimide, a viscous oil was obtained, which was purified by extracting it several times with light petroleum. It was dried first at 80° for a short time, and finally over solid potassium hydroxide under diminished pressure. On cooling to 0° it was obtained as a brittle solid which became viscous at the ordinary temperature.

Intramolecular Rearrangement of n-*Butylaniline.*

The experimental details for the production of 4-amino-*n*-butylbenzene have already been described (p. 110), and it has been mentioned that other substances are produced in the reaction. The primary amines which were separated by the use of zinc chloride were distilled. Aniline was obtained in the first fractions, the amount being dependent on the experimental conditions. The principal fraction was 4-amino-*n*-butylbenzene, but there was still a residue of amines boiling at above 270°; this, on distillation, proved to be a complex mixture, from which a primary amine boiling at 295—300° was isolated, and was probably 4-*amino*-1 : 3-*di*-n-*butylbenzene*:

0·0900 gave 5·3 c.c. N_2 at 20° and 737 mm. $N = 6·7$.

$C_{14}H_{23}N$ requires $N = 6·8$ per cent.

It yields a sparingly soluble *sulphate*, and after treatment with nitrous acid in the cold, combines with alkaline β-naphthol with the formation of an *azo*-compound. A fraction of still higher boiling point which also contains a primary amine was not investigated.

The ethereal washings of the zincichloride (p. 110) obtained by the action of *n*-butyl alcohol on aniline zincichloride were shaken with dilute sodium hydroxide solution to remove a portion (*A*) containing phenolic substances and then several times with dilute hydrochloric acid to remove a portion (*B*) containing secondary and tertiary amines. There was finally obtained an ethereal solution containing for the most part substances which are soluble only in concentrated hydrochloric acid, and are precipitated on dilution. These substances boil at above 290° under the ordinary pressure, and their sulphuric solution in the presence of nitrous acid develops an intense bluish-black colour. The behaviour and properties of these substances suggest that they may be diphenylamine derivatives, but they were not further investigated. The separated portions were examined as follows: (*A*) The phenolic substances were isolated by acidifying the alkaline solution and extracting with ether. They appeared to be a mixture of phenol and butylphenol, for on distillation two definite fractions were obtained, one at about 200—210°, and the principal fraction at 240—245°. These phenols do not appear to be constant constituents of the products of the reaction being usually present at the most in small amounts.

(*B*) The amines on distillation gave a secondary amine boiling at 235—245°, with small amounts of a primary amine at 255—265°, which was shown to be 4-amino-*n*-butylbenzene. Between 275° and 290° a secondary amine, probably 4-n-*butylamino*-n-*butylbenzene*, was collected in an impure condition. It was dissolved in dilute hydrochloric acid and treated with nitrous acid, when 4-n-*butyl-phenyl*-n-*butylnitrosoamine* separated as a yellowish-red oil, volatile in steam, and having a pleasant odour:

0·0703 gave 7·4 c.c. N_2 at 17·8° and 744 mm. $N = 12·1$.

$C_{14}H_{22}ON_2$ requires $N = 12·0$ per cent.

The amount of this secondary amine present in the mixture resulting from the action of *n*-butyl alcohol on aniline zincichloride is usually small, and the yield appears to depend on the experimental conditions. The residue of higher boiling point yielded, at about 300°, aminodibutylbenzene, which was isolated as a sparingly soluble sulphate, and a mixture of amines, yielding fractions up to 360°. Amines of still higher boiling points were obtained on dis-

REARRANGEMENT OF THE ALKYLARYLAMINES. 125

tilling under diminished pressure until only a semi-carbonised mass remained in the flask. This distillate, which contained primary, secondary, and tertiary amines, was not further investigated, but no doubt consisted of amino-compounds containing more than two butyl groups in the nucleus.

The formation of 4-amino-n-butylbenzene by the action of dry n-butyl alcohol on aniline zincichloride may be due to the initial formation of n-butylaniline, followed by intramolecular change, or to the direct entry of the butyl group into the nucleus. The former suggestion agrees better with the experimental results, for by reducing the time of the reaction and the temperature at which it occurs n-butylaniline is obtained in greater amount than usual, whilst the yield of 4-amino-n-butylbenzene is much smaller. In one experiment the temperature was allowed to rise gradually to 180—200° over a period of six hours. The products were aniline and n-butylaniline, only a small quantity of 4-amino-n-butylbenzene being formed.

It was also found that pure n-butylaniline, in the presence of zinc chloride and also certain other salts, underwent intramolecular change on heating at temperatures between 200° and 240° for about six to eight hours.

n-*Butylaniline and Cobalt Chloride*.

n-Butylaniline (4·5 grams) was heated in a sealed tube at temperatures between 200° and 240° for seven hours with anhydrous cobalt chloride (2 grams). There was only a slight pressure on opening the tube, and the contents, which were initially pale green, changed to a deep blue, crystalline mass. After treatment with warm water and dilute sodium hydroxide solution the mixture of amines had the following composition :

Primary amine ...	...	...	...	...	62 per cent.
Secondary amine	...	...	...	...	14 ,, ,,
Bases insoluble in dilute hydrochloric acid ...				23	,, ,,

The primary amine gave an acetyl compound melting at 103° after one crystallisation, which was identical with 4-acetylamino-n-butylbenzene.

Other experiments were carried out, by heating pure n-butylaniline under pressure in the presence of various substances, such as zinc chloride and sodium chloride. The results obtained are given in the following table:

Substance. added.	Duration of heating.		Percentage composition of resulting amines.		
			Primary.	Secondary.	Insoluble in dilute acid.
—	8 hours.		1	99	—
NaCl	8	,,	—	100	—
SiO_2	8	,,	1	99	—
$CaSO_4$	8	,,	—	100	—
$CaCl_2$	8	,,	2	98	—
$CoCl_2$	7	,,	62	14	23
$CuCl_2$	8	,,	11	*	50
$ZnCl_2$	7	,,	47	37	16
$CoCl_2$	8	,,	50	20	30
$HgCl_2$	8	,,	20	*	●

* Not determined.

The temperature in every case varied between 200° and 240° except in the case of *n*-butylaniline, which was heated alone at 240—260°. The experiments are, however, not comparable. When the amine was heated with cupric chloride the mixture at the end of the reaction was very dark and contained small, bright red, metallic particles, presumably of copper. The yield of amines insoluble in dilute hydrochloric acid was also high. In the experiment with mercuric chloride some metallic mercury was obtained.

It was observed that the intramolecular rearrangement of the butylaniline was accompanied by the combination of the secondary amine with the substance added. Some of these additive compounds have been isolated.

n-*Butylaniline cobaltochloride* was obtained by heating butylaniline with an excess of finely powdered anhydrous cobalt chloride in the presence of chloroform. After collecting the excess of suspended metallic salt, the chloroform solution was evaporated to dryness, when the cobaltochloride was obtained as a greenish-blue, vitreous mass, which becomes viscous after heating at 100°. It is decomposed by water with the formation of cobalt chloride and butylaniline :

0·4226 gave 0·4265 AgCl. Cl = 25·0.
$C_{10}H_{15}N,CoCl_2$ requires Cl = 25·4 per cent.

n-*Butylaniline zincichloride* was obtained as a grey, vitreous mass by heating *n*-butylaniline in chloroform solution with an excess of zinc chloride. The solution was filtered from the zinc chloride and the solvent removed by distillation. On washing with small quantities of light petroleum to remove the excess of butylaniline, the zincichloride remained in a pure condition :

0·1450 gave 0·1458 AgCl. Cl = 24·9.
$C_{10}H_{15}N,ZnCl_2$ requires Cl = 24·9 per cent.

n-Butylaniline and cadmium chloride also form an additive com-

pound, which in common with those of the chlorides of cobalt and zinc is readily decomposed by hot water. The instability of the zincichloride toward water explains the readiness with which primary amines may be separated from secondary by the use of zinc chloride.

Evidence was obtained of the formation of compounds with ferric chloride and cupric chloride by warming the chlorides with a chloroform solution of butylaniline. With ferric chloride a very dark green substance was obtained, soluble in aqueous alcohol (75 per cent.), giving a bright green colour. Cupric chloride gave a deep violet chloroform solution, yielding a solid which was almost black.

With the chlorides of calcium or sodium, or with calcium sulphate and silica, no indications were obtained of the formation of additive compounds.

Additive Compounds of 4-Amino-n-butylbenzene with Metallic Salts.

The products of intramolecular change apparently contained additive compounds of the primary amine with the salt employed. A few of these compounds were prepared and analysed.

4-*Amino*-n-*butylbenzene zincichloride* was obtained as a caseous mass by adding an aqueous solution of zinc chloride to 4-amino-*n*-butylbenzene :

0·2355 gave 0·1540 AgCl. $Cl = 16·2$.

$(C_{10}H_{15}N)_2ZnCl_2$ requires $Cl = 16·3$ per cent.

It is sparingly soluble in water, alcohol, or ether. Dilute acids hydrolyse it rapidly.

4-*Amino*-n-*butylbenzene cobaltochloride* was prepared by mixing alcoholic solutions of anhydrous cobalt chloride with an excess of the base. After being crystallised from absolute methyl alcohol, it formed a bright blue powder which is decomposed by water into its components, slowly in the cold, but more quickly on warming :

0·0858 gave 0·0562 AgCl. $Cl = 16·2$.

0·2155 ,, 0·0793 $CoSO_4$. $Co = 14·0$.

$(C_{10}H_{15}N)_2,CoCl_2$ requires $Cl = 16·6$; $Co = 13·8$ per cent.

4-*Amino*-n-*butylbenzene cadmichloride* was obtained as a white, bulky mass by mixing the components in methyl-alcoholic solution. It crystallises from hot methyl alcohol in small, white crystals with a nacreous lustre, and tends to form crusts of crystals on the surface of the solution. It is hydrolysed on boiling with water.

Action of Heat on n-Butylaniline Hydrochloride.

Crude mono-*n*-butylaniline was converted into its hydrochloride by evaporating it with an excess of concentrated hydrochloric acid until the solution was of a syrupy consistency. On keeping overnight it had solidified to a hard mass of crystals, which were transferred to a retort and heated in an oil-bath at 260—300°. The disengaged vapours were passed through a condenser to remove any liquid. A considerable amount of a liquid was condensed, nearly all of which boiled between 80° and 83°, indicating the presence of *n*-butyl chloride. The gas which escaped condensation was passed through bromine, and after removing the excess of bromine by means of sodium hydrogen sulphite, a small amount of a colourless liquid was obtained, which was not further examined. In this experiment an excess of hydrochloric acid was originally present. Another experiment was carried out taking precautions to avoid an excess. The hydrochloride was dried on a steam-bath for twelve hours, and exposed to the air for a further period, after which it was heated at 280—300° for one hundred hours. During the earlier stages of the experiment, a liquid (*A*) was condensed, which became darker as the heating proceeded. The gas evolved was passed through bromine, when a liquid dibromide was obtained in small amount.

From the distillate (*A*) there separated a small quantity of flat, grey crystals, which consisted of aniline hydrochloride. The liquid portion, after being rendered alkaline, gave, on distillation, a fraction boiling between 70° and 80°, chiefly at 77—80°, which was *n*-butyl chloride. There was also a fraction boiling chiefly between 200° and 250°, containing principally a primary amine mixed with some secondary, the former being identified as aniline.

The residue in the flask, which was black and tarry, was rendered alkaline, and the resulting amine treated with an excess of zinc chloride solution, in order to separate the primary amines from the other products. The insoluble zincichlorides gave a mixture of amines boiling between 200° and 255°, and yielding a considerable fraction at 240—255°. The ethereal washings of the zincichloride contained a secondary amine, boiling between 230° and 250°, whilst at 250—260° a mixture of primary and secondary amines was obtained. There were also present bases which were insoluble in dilute hydrochloric acid, but soluble in the concentrated acid, and were probably diphenylamine derivatives.

Preparation of n-Butylaniline Hydrochloride.

n-Butylaniline hydrochloride has previously been obtained by Kahn (*Ber.*, 1885, **18**, 3361) by evaporating a solution of *n*-butyl-

aniline in hydrochloric acid to crystallisation. A more convenient method was to pass a stream of dry hydrogen chloride into a solution of butylaniline in an equal volume of benzene or toluene. A considerable amount of heat was generated, sufficient to evaporate some of the hydrocarbon. On cooling, n-butylaniline hydrochloride crystallised out, and was collected, washed, and dried. The filtrate, which still contained much of the salt, was precipitated by the addition of ether, when the hydrochloride was obtained in very small, white crystals having a silvery appearance. They were collected, washed with further amounts of ether, and dried, first at 60° and later at 100°.

n-Butylaniline hydrochloride crystallises in very small, irregular plates from hot ethyl acetate, in which it is readily soluble. It is only moderately soluble in the cold solvent.

Comparative Experiments on Alkylarylamines with various Alkyl Groups.

A comparison was made of the stability of alkylarylamines containing alkyl groups of different weight. For this purpose methyl- and n-butyl-arylamines were employed. In the earlier investigations the experiments were carried out on the intramolecular rearrangement of methyl- and n-butyl-aniline. The secondary amines were heated in sealed tubes with a molecular proportion of substances which aid the formation of aminoalkylbenzenes. The tubes were arranged in iron shields in such a manner that the temperature and the duration of heating were approximately the same in each case. The results are given in the following table. The results show that there is a difference, although not very marked, in the behaviour of the two amines, n-butylaniline undergoing intramolecular change more readily. In this case the action is characterised by the formation of appreciable quantities of substances of the nature of diphenylamine, which are either absent in the case of methylaniline or present only in small amount.

		n-Butylaniline.		Methylaniline.	
Substance. added.	Time of heating.	Primary. Per cent.	Secondary. Per cent.	Primary. Per cent.	Secondary. Per cent.
$CoCl_2$	5 hours.	73	10	57	32
$CdCl_2$	6 ,,	52	24	43	24
HCl	6 ,,	*	20	—	95
HCl	8 ,,	68	18	23	*
$CoCl_2$ ($\frac{1}{2}$ mol.)	5 ,,	*	33	*	50
HCl	4 ,,	*	33	*	49

* Not estimated.

It was observed that methylaniline yields additive compounds with cobalt chloride, zinc chloride, and cadmium chloride similar to those described in the case of *n*-butylaniline (p. 126).

Methylaniline cobaltochloride was obtained as a dull blue powder on triturating anhydrous cobalt chloride with an excess of freshly distilled methylaniline and heating the mixture on a steam-bath for a short time, the excess of methylaniline being then extracted by means of chloroform. On long keeping, the salt became greenish-yellow :

0·1157 gave 0·1402 AgCl.   Cl = 30·0.

0·4312 ,, 0·2818 $CoSO_4$.   Co = 24·9.

$C_7H_7N,CoCl_2$ requires Cl = 30·2 ; Co = 25·1 per cent.

Methylaniline cadmichloride was prepared in a similar way. It is a white powder, which is decomposed by water :

0·4099 gave 0·4016 AgCl.   Cl = 24·2.

0·3045 ,, 0·2150 $CdSO_4$.   Cd = 39·0.

$C_7H_7N,CdCl_2$ requires Cl = 24·6 ; Cd = 39·0 per cent.

In the formation of the additive compounds of alkylanilines with metallic salts, the steric effects of the alkyl group may affect the formation of the compounds to a different extent, and for this and other reasons (difficulty of ensuring the same temperature and pressure in each tube) the experiments are probably not strictly comparable. The comparison of the relative stability of methyl and *n*-butyl groups was therefore carried out with tertiary amines, such as methyl-*n*-butylaniline. The intramolecular rearrangement of this compound proceeds in two stages, namely, the formation of a secondary amine, followed by conversion into a primary amine. It therefore became necessary to prepare the compounds that may possibly occur in the mixture.

*Methyl-*n-*butylaniline.*

This substance was prepared in three ways, namely, by the interaction of (*a*) *n*-butyl bromide and methylaniline, (*b*) *n*-butyl chloride and methylaniline, (*c*) methyl iodide and *n*-butylaniline, and the products in each case were the same. It was found that to obtain pure methyl-*n*-butylaniline by distillation was a tedious operation leading to losses. In the earlier work the process of purification consisted in converting the crude methyl-*n*-butylaniline into its picrate, and then crystallising the picrate until pure. This procedure was abandoned later and the secondary amine was removed by heating the crude tertiary amine with a slight excess of the theoretical amount of phenylcarbimide. The excess of the reagent was removed by warming with water, followed by distillation in a cur-

rent of steam. *Methyl-n-butylaniline* was obtained in this way as a pale yellow, refractive liquid boiling at 242—$243°/766$ mm.:

$0·1071$ gave $0·3180$ CO_2 and $0·0987$ H_2O. $C = 81·0$; $H = 10·3$.

$0·0988$,, $7·7$ c.c. N_2 at $28°$ and 748 mm. $N = 8·8$.

$C_{11}H_{17}N$ requires $C = 80·9$; $H = 10·5$; $N = 8·6$ per cent.

The *hydrochloride* was obtained as an oil on passing a stream of dry hydrogen chloride into an ethereal solution of the base. After repeated washings with small quantities of dry ether, and keeping over potassium hydroxide under diminished pressure, it solidified to a mass of white, glistening laminæ:

$0·1633$ gave $0·1170$ AgCl. $Cl = 17·7$.

$C_{11}H_{17}N,HCl$ requires $Cl = 17·8$ per cent.

It is extremely soluble in water or alcohol, moderately so in nitrobenzene, and sparingly so in toluene.

From an aqueous solution of the hydrochloride containing a slight excess of free acid, the *platinichloride* was obtained as an orange-yellow precipitate sparingly soluble in water:

$0·1152$ gave $0·0304$ Pt. $Pt = 26·4$.

$0·2234$,, $7·0$ c.c. N_2 at $18°$ and 738 mm. $N = 3·6$.

$(C_{11}H_{17}N)_2,H_2PtCl_6$ requires $Pt = 26·5$; $N = 3·8$ per cent.

The *picrate* crystallises from a methyl-alcoholic solution of the components in small, yellow crystals melting at $90°$.

Titration with Titanous Chloride.—$0·010$ required $20·3$ c.c. $TiCl_3$ (1 c.c. $TiCl_3 = 0·001257$ gram Fe). Calc. as $C_{11}H_{17}N,C_6H_3O_7N_3 = 100·5$ per cent.

The melting point of this compound differs from that recorded by Komatsu (*loc. cit.*), who gives 141—$142°$. The picrates from the amine obtained by introducing the alkyl groups in different order were found to be identical, and a mixture of them also melted at $90°$.

p-*Nitrosomethyl-n-butylaniline.*—Nitrous acid acted on a solution of methyl-*n*-butylaniline hydrochloride containing free hydrochloric acid yielding a reddish-brown solution, and the addition of ice-cold dilute aqueous ammonia precipitated the base as an oil, which was removed by means of ether. It was obtained as a greenish-blue liquid, which was steel-blue by reflected light:

$0·1184$ gave $0·2981$ CO_2 and $0·0909$ H_2O. $C = 68·7$; $H = 8·5$.

$0·1282$,, $16·2$ c.c. N_2 at $15°$ and 745 mm. $N = 14·8$.

$C_{11}H_{16}ON_2$ requires $C = 68·7$; $H = 8·4$; $N = 14·6$ per cent.

On heating the base under reflux with an excess of a 10 per cent. aqueous solution of sodium hydroxide, decomposition occurred with the production of a volatile amine, probably methyl-*n*-butylamine.

4-*Methylamino-n-butylbenzene* was obtained by heating 4-amino-

n-butylbenzene with methyl iodide. The addition of a dilute solution of sodium hydroxide liberated the base as an almost colourless oil boiling at 262—265°/760 mm.:

0·1042 gave 7·6 c.c. N_2 at 15° and 759 mm. $N = 8·7$.

$C_{11}H_{17}N$ requires $N = 8·6$ per cent.

By the action of nitrous acid 4-n-*butylphenylmethylnitrosoamine*, $C_{11}H_{16}ON_2$, was obtained as a pale yellow oil. This was nitrated by dissolving it in glacial acetic acid, and cautiously adding ten times its weight of fuming nitric acid in the cold. After a short time the reaction was completed by heating on the water-bath until the mixture was pale red or yellow. This was then poured on crushed ice, and the nitro-derivative collected and crystallised by dissolving it in cold fuming nitric acid. On keeping, *dinitro*-n-*butylphenyl*-4-*methylnitroamine*, $C_{11}H_{14}O_6N_4$, was obtained in pale yellow plates. From warm glacial acetic acid it crystallises in very pale yellow, glistening plates at 86°.

Ethyl-n-*butylaniline* was obtained by the action of *n*-butyl chloride on ethylaniline and also by allowing ethyl iodide to react with butylaniline. It was obtained pure in the manner described for methylbutylaniline, and is a pale yellow oil boiling at 248°/768 mm.:

0·0968 gave 0·2880 CO_2 and 0·0891 H_2O. $C = 81·1$; $H = 10·2$.

0·0836 ,, 5·9 c.c. N_2 at 25° and 748 mm. $N = 8·0$.

$C_{12}H_{19}N$ requires $C = 81·3$; $H = 10·8$; $N = 7·9$ per cent.

The *picrate* crystallises from aqueous alcohol in bright yellow, thin prisms or narrow plates melting at 100°:

0·010 required 20·0 c.c. $TiCl_3$ (1 c.c. $TiCl_3 = 0·00125$ gram Fe). Calc. for $C_{12}H_{19}N, C_6H_3O_7N_3 = 99·3$ per cent.

p-*Nitrosoethyl*-n-*butylaniline* was obtained as an oil having a dark blue, metallic colour when viewed by reflected light:

0·017 gave 12·1 c.c. N_2 at 24° and 741 mm. $N = 13·7$.

$C_{12}H_{18}ON_2$ requires $N = 13·6$ per cent.

p-*Nitrosoethyl*-n-*butylaniline zincichloride* was prepared by mixing alcoholic solutions of the components and evaporating the alcohol under diminished pressure, but it was not obtained crystalline.

4-*Ethylamino*-n-*butylbenzene* is a liquid of agreeable odour and boiling at 270—272°/762 mm.:

0·1024 gave 7·5 c.c. N_2 at 22° and 746 mm. $N = 8·2$.

$C_{12}H_{19}N$ requires $N = 7·9$ per cent.

The *nitrosoamine* is a yellow oil:

0·0999 gave 11·65 c.c. N_2 at 20° and 746 mm. $N = 13·4$.

$C_{12}H_{18}ON_2$ requires $N = 13·6$ per cent.

2-*Amino*-5-n-*butyltoluene.*

Molecular proportions of *n*-butyl alcohol and *o*-toluidine were heated at 200—240° for twenty-four hours, and the mixture was treated in the manner already described for 4-amino-*n*-butylbenzene. 2-*Amino*-5-n-*butyltoluene* was obtained as a very pale yellow liquid boiling at 265—268°/765 mm.:

0·0960 gave 7·1 c.c. N_2 at 20° and 757 mm. $N = 8·6$.
$C_{11}H_{17}N$ requires $N = 8·6$ per cent.

The *hydrochloride* crystallises from warm dilute hydrochloric acid in rosettes of white needles:

0·1176 gave 0·0840 AgCl. $Cl = 17·8$.
$C_{11}H_{17}N,HCl$ requires $Cl = 17·8$ per cent.

It is precipitated from aqueous solution by the addition of an excess of hydrochloric acid.

The *acetyl* derivative crystallises from dilute aqueous alcohol in white masses of crystals melting at 89°:

0·1039 gave 6·0 c.c. N_2 at 15° and 750 mm. $N = 6·8$.
$C_{13}H_{19}ON$ requires $N = 6·8$ per cent.

On diazotising the hydrochloride and adding the solution to alkaline β-naphthol, 5-n-*butyltoluene*-2-*azo*-β-*naphthol* is precipitated. It crystallises from hot glacial acetic acid in bulky masses of small, bright red needles melting at 105—107°. It is only moderately soluble in alcohol, and dissolves in concentrated sulphuric acid with the production of a purple coloration.

4-*Amino*-3-n-*butyltoluene.*

This amine was obtained by the action of *n*-butyl alcohol on *p*-toluidine zincichloride, in the manner already described for the preparation of 4-amino-*n*-butylbenzene. It is a liquid boiling at 265—270° under atmospheric pressure:

0·1496 gave 11·3 c.c. N_2 at 19° and 762 mm. $N = 8·9$.
$C_{11}H_{17}N$ requires $N = 8·6$ per cent.

The *acetyl* derivative separates as a white mass on cooling the product of interaction of 4-amino-3-*n*-butyltoluene and acetic anhydride. It crystallises from alcohol in tufts of white, slender needles melting at 129°:

0·1113 gave 0·3105 CO_2 and 0·0953 H_2O. $C = 76·1$; $H = 9·5$.
$C_{13}H_{19}ON$ requires $C = 76·0$; $H = 9·3$ per cent.

The Intramolecular Rearrangement of Methyl-n-butylaniline.

Pure methyl-n-butylaniline was heated in a sealed tube with one molecular proportion of either zinc chloride or cobalt chloride. In one experiment methyl-n-butylaniline hydrochloride was employed. The temperature varied between 200° and 250°, and the heating was allowed to continue for about six to eight hours. On opening the tubes there was usually a pressure due to the presence of an inflammable gas. The contents of the tube were rendered alkaline, and the amines were obtained by distillation in a current of steam. The mixture of amines obtained in this way was treated with zinc chloride solution, which removed the bulk of the primary amines. The ethereal washings of the zincichloride were washed with dilute hydrochloric acid to remove primary, secondary, and tertiary amines. From this acid solution the secondary amines were separated as nitrosoamines and the primary amines converted into the corresponding diazonium salts.

The nitrosoamines separated in this way were nitrated, yielding in each case an oily product, which was obtained crystalline only on keeping in contact with concentrated nitric acid for several days. By pressing on a porous tile to remove oily impurities, and by repeated recrystallisation from glacial acetic acid, a small amount of a pale yellow, crystalline substance was obtained melting at 93°, and the melting point was raised to 94—95° by the addition of 3 : 5-dinitro-p-tolyl-n-butylnitroamine. It is probable that the latter compound was present in the nitration product, indicating the existence of n-butyl-p-toluidine in the mixture of amines from the intramolecular rearrangement of methyl-n-butylaniline. It was not found possible to isolate any other nitro-compound in a pure state from the mixture, although appreciable amounts were present.

It is probable that in the mixture dinitro-n-butylphenylmethylnitroamine was also present, as only n-butyl-p-toluidine and 4-methylamino-n-butylbenzene would be expected to occur in any appreciable amount.

In one case small amounts of 2 : 4 : 6-trinitrophenylmethylnitroamine were isolated, and the primary amine from it indicated p-toluidine. By crystallisation of the azo-compounds from this experiment, p-tolueneazo-β-naphthol, melting at 129°, was isolated, and this melting point was not depressed by the addition of pure p-tolueneazo-β-naphthol. The small amounts of derivatives of methylaniline and p-toluidine isolated were due probably to the rearrangement not proceeding to completion.

*Action of Heat on Methyl-*n-*butylaniline Hydrochloride.*

Methyl-*n*-butylaniline (4·2 grams) was dissolved in an excess of concentrated hydrochloric acid in a small glass retort, which was heated in an oil-bath at 150—200°, a stream of hydrogen chloride being allowed to pass through the retort during the period of heating. A portion of the residue in the vessel was removed, and after diluting and adding more hydrochloric acid it was cooled to 0° and treated with a slight excess of an aqueous solution of sodium nitrite. A nitrosoamine separated, which was removed by extraction with ether. The ethereal solution was washed several times with water and dilute sodium hydroxide, dried, and evaporated, and the residue was dissolved in glacial acetic acid, nitrated by heating it on a water-bath with fuming nitric acid, until the colour of the mixture had changed to a pale red. On pouring the mixture into water an oily product was obtained which, when crystallised from fuming nitric acid, melted at 90—92°. The addition of trinitrophenylbutylnitroamine (m. p. 99°) depressed the melting point to about 89—92°, whilst the addition of trinitrophenylmethylnitroamine raised the melting point to 110—115°. The secondary amine resulting from the elimination of alkyl groups from methylbutylaniline in a stream of hydrogen chloride is therefore probably a mixture of methyl- and butyl-aniline.

The further examination of the products of this reaction is deferred until the physical constants of mixtures of trinitrophenylmethylnitroamine and trinitrophenylbutylnitroamine have been determined.

The Nitration of Dialkylanilines.

The method usually adopted to nitrate dissimilarly substituted dialkylanilines was to add cautiously about 10 to 15 times their weight of fuming nitric acid to a solution in glacial acetic acid. The reaction was completed by heating on the water-bath until the dark colour of the mixture had given place to a pale yellow or red. The nitration product was then isolated by pouring on ice, when it was collected and purified by crystallisation from fuming nitric acid.

Dibutylaniline, when treated in this way, gave *trinitrophenyl-*n-*butylnitroamine* in very pale yellow plates melting at 100°:

0·1093 gave 20·3 c.c. N_2 at 20° and 748 mm.   N = 21·3.

$C_{10}H_{11}O_8N_5$ requires N = 21·3 per cent.

It is soluble in alcohol or acetone, and can be conveniently recrystallised from hot glacial acetic acid. An alcoholic solution of

sodium hydroxide in the cold gives a deep orange-red coloration. It dissolves in cold concentrated sulphuric acid without any development of colour, but on dilution a yellow turbidity is produced.

This substance was shown to be identical with the nitro-derivative obtained on nitrating phenyl-*n*-butylnitrosoamine. It was also obtained by nitrating dibutylaniline in the presence of nitric and sulphuric acids. Dibutylaniline (10 grams) dissolved in concentrated sulphuric acid (18 grams) was slowly added to a mixture of sulphuric (50 grams) and nitric acids (150 grams), the temperature being maintained between 35° and 45° throughout the reaction. After all the amine had been added the mixture was maintained for some time at 50°, and then thrown on crushed ice, when the nitro-compound was collected as a viscous, red substance and purified in the usual manner by crystallisation from fuming nitric acid. The strongly acid aqueous portion was found to contain butyric acid. The nitro-compound was removed by filtration through a thick layer of glass-wool. It was found necessary to take these precautions to remove the last traces of the nitro-compound in order to prevent contamination of the products at a later stage. To the acid filtrate, iron filings were added gradually, care being taken to avoid a too-vigorous action. After remaining overnight, the solution was distilled in a current of steam. The distillate, which still contained a small amount of nitric acid, was neutralised and evaporated to a small bulk. It was then rendered acid by adding an excess of sulphuric acid, and the last traces of nitric acid were removed by a further treatment with iron filings. A further distillation in a current of steam gave a distillate which contained a volatile acid, and this was identified by means of its "distillation constant" determined in an apparatus described by the authors (*Sci. Proc. Roy. Dubl. Soc.*, 1919, **15**, 513). The constant agreed with that for *n*-butyric acid mixed with a small proportion of an impurity, and its presence was confirmed by its odour and by its reaction with ferric chloride.

Comparative experiments were also carried out, using dimethyl-aniline. Methyl-*n*-butylaniline was nitrated by fuming nitric acid dissolved in glacial acetic acid following the method described above. The product melted at 123—125° after crystallisation from fuming nitric acid. It was recrystallised from glacial acetic acid, and was found to be identical with 2 : 4 : 6-trinitrophenylmethylnitroamine, for no depression of the melting point occurred when a mixture was prepared with this nitro-compound and trinitrophenylmethylnitro-amine from another source.

Ethyl-*n*-butylaniline, on nitration with fuming nitric acid or with

a mixture of nitric and sulphuric acids, gave a product which, on crystallisation from fuming nitric acid, furnished a mixture yielding trinitrophenyl-*n*-butylnitroamine on crystallisation from glacial acetic acid.

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