235. *Rearrangement of the Alkylanilines. Part VIII. Migration of Large Groups.*

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In earlier Parts (J., 1920, **117**, 103; 1927, 64; 1930, 1558, 1566; 1932, 2396) it was shown that monoalkylanilines, with *n*-alkyl groups from ethyl to butyl, smoothly underwent rearrangement on heating with suitable metal halides to form *p*-aminoalkylbenzenes. The work now described was undertaken with the object of determining the limits of this type of rearrangement. *n*-Amyl-, *n*-hexyl-, *n*-heptyl-, *n*-octyl-, *n*-dodecyl-, and cetyl-aniline were used for this purpose. When they are heated with anhydrous cobalt chloride or bromide at 212°, the alkyl group is transferred to the nucleus with no noticeable elimination as olefin. From the rearrangement of *n*-octylaniline, an amine is obtained which is identical with that established by Beran (*Ber.*, 1885, **18**, 132) to be *p*-amino-*n*-octylbenzene. The rearrangement of cetylaniline gives an amino-hexadecylbenzene, which from its m. p. and that of its acetyl derivative is probably identical with the aminocetylbenzene described by Krafft (*Ber.*, 1886, **19**, 2984) in which the alkyl group has the normal configuration. The orientation of the amino-group with respect to the cetyl has been found to be *para* by conversion of the amine into *p*-hydroxycetylbenzene (Krafft, *Ber.*, 1888, **21**, 3181; Hickinbottom, unpublished observation).

It is evident that when *n*-octyl or the cetyl group is transferred from the amino-group to the nucleus under the conditions described in this paper, it enters the *p*-position with respect to the amino-group and the configuration of the alkyl group is unchanged. It appears justifiable to assume from these examples that similar regularities occur in the rearrangements of other *n*-alkylanilines. This generalisation is rendered more probable by the proof (J., 1920, **117**, 110; 1930, 1558, 1566; 1932, 2396) that alkylanilines containing smaller alkyl groups such as *n*-propyl, *n*- and *iso*-butyl, and *iso*amyl suffer rearrangement under the influence of cobalt chloride or bromide without any alteration in the configuration of the alkyl group, which takes up a position in the nucleus *para* to the amino-group. Migration of the alkyl group to the *o*-position was not detected, although it is not improbable that it may occur to a limited extent.

More satisfactory evidence of the transference of the mobile group to a position other than *para* was observed with benzylaniline and with *cyclo*hexylaniline. Both these amines furnished not only the *p*-compound on rearrangement, but appreciable yields of isomeric amines in which the group is assumed to have entered the *o*-position. There was also good evidence of a similar type of rearrangement with *sec.*-octylaniline.

The most striking difference in behaviour of both *cyclo*hexylaniline and *sec.*-octylaniline as compared with the *n*-alkylanilines was the elimination of the greater part of the *cyclo*hexyl or the *sec.*-octyl group as unsaturated hydrocarbon. In this, they show a behaviour intermediate between that of the alkylaniline with *tert.*-alkyl groups and those with *n*-alkyl chains (this vol., p. 404).

Under the experimental conditions employed, the rearrangement is not confined to the formation of *o*- and *p*-aminoalkylbenzenes. Considerable amounts of products of higher boiling point are formed, consisting chiefly of alkylaminoalkylbenzenes $NHR{\cdot}C_6H_4R$. Benzylaniline, however, gives a higher-boiling fraction consisting largely of 2 : 4-*dibenzylaniline*.

The formation of such compounds may be caused by the preliminary formation of dialkylaniline and its subsequent rearrangement:

$$2NHR{\cdot}C_6H_5 \longrightarrow NH_2{\cdot}C_6H_5 + NR_2{\cdot}C_6H_5 \longrightarrow NHR{\cdot}C_6H_4R$$

Alternatively the reaction may be represented by assuming that the alkyl group during its migration from the nitrogen to the nucleus may attack unchanged alkylaniline with the formation of an alkylaminoalkylbenzene.

The validity of these hypotheses depends on the absence of dialkylaniline in the secondary amine used for the rearrangement. Special precautions were taken to ensure this (cf. J., 1930, 933). Furthermore, crystalline secondary amines, such as dodecylaniline and cetylaniline, which can very easily be freed from tertiary amines, furnish alkylaminoalkylbenzenes in yields amounting to 40—55% of the weight of starting material. Benzylaniline, also easily purified, similarly yields a high proportion of 2 : 4-dibenzylaniline.

The simplest explanation of the formation of such products is a preliminary conversion of some of the secondary amine into aniline and a dialkylaniline. Support for this view is afforded by the detection of tertiary amines in the products of rearrangements promoted by metal salts (J., 1927, 64; unpublished observations). A similar reaction has been detected when the secondary amine is heated as its hydrogen halide salt (Beckmann and Correns, *Ber.*, 1922, **55**, 852), and the reverse change of dialkylaniline to monoalkylaniline occurs when dimethylaniline is heated with aniline hydrochloride (Frankland, Challenger, and Nicholls, J., 1919, **115**, 203).

During the course of this work the interesting observation was made that the hydrochlorides of the alkylaminoalkylbenzenes and to a less extent the hydrochlorides of the alkylanilines described in this paper, have abnormal solubilities; n-*heptylamino*-n-*heptylbenzene hydrochloride*, for example, is soluble in light petroleum (b. p. 40—60°). A more detailed description of the reactions of these substances is reserved for a future paper.

EXPERIMENTAL.

The general conditions for effecting the rearrangement consisted in heating the secondary amine with anhydrous cobalt chloride or bromide in a long tube having free access to the air at its upper end through an efficient guard-tube. The mixture was heated at a constant temperature by a vapour-bath. A sufficient length of the upper part of the tube was exposed to the air to serve as a condenser.

The product was isolated by treatment with aqueous ammonia, extraction with ether, and distillation of the extract under reduced pressure; three main fractions were generally obtained: (*a*) aniline; (*b*) a mixture of aminoalkylbenzene and unchanged secondary amine; (*c*) a fraction of higher b. p., which in most rearrangements consisted largely of an alkylaminoalkylbenzene. The residue, generally small, was not examined.

The aniline was identified by its b. p. and acetyl derivative. The major constituents of fraction (*b*) were separated by aqueous zinc chloride. The identity of the secondary amine was established by the comparison of suitable crystalline derivatives with authentic specimens. The aminoalkylbenzene from this fraction was generally purified through its sulphate or its acetyl derivative. The separation of the major constituent of fraction (*c*) in a pure state was usually achieved by repeated fractionation under reduced pressure, sometimes followed by crystallisation of its hydrochloride.

Rearrangement of n-*Amylaniline*.—*n*-Amylaniline was prepared by heating 87 g. of *n*-amyl bromide with 140 g. of aniline in a water-bath for 8 hours. The mixture was made alkaline, aniline removed as the sparingly soluble zincichloride (J., 1930, 992), and the unprecipitated amine isolated. Fractional distillation yielded 57 g. of *n*-amylaniline (b. p. 127—128°/16 mm.) and 14 g. of crude di-*n*-amylaniline (b. p. 260—280°). The *p*-toluenesulphonyl derivative of the former crystallised from alcohol in felted needles, m. p. 74° (v. Braun and Murjahn, *Ber.*, 1926, **59**, 1204, give m. p. 76—77°).

p-*Amino*-n-*amylbenzene*, b. p. 130°/16 mm., was a colourless liquid of not unpleasant odour (Found: C, 80·7; H, 10·5; N, 8·4. $C_{11}H_{17}N$ requires C, 80·9; H, 10·5; N, 8·6%). The *hydrochloride* separated as a felted mass of needles on cautious addition of hydrochloric acid to its aqueous solution (Found: HCl, 18·4. $C_{11}H_{17}N,HCl$ requires HCl, 18·3%). The sulphate was sparingly soluble in cold water, but crystallised from hot water in small white platelets. The *acetyl* derivative separated from aqueous alcohol in nacreous platelets, m. p. 101° (Found: C, 76·3; H, 9·2. $C_{13}H_{19}ON$ requires C, 76·0; H, 9·3%). The p-*toluenesulphonyl* derivative, prepared from the amine and *p*-toluenesulphonyl chloride in pyridine solution, separated from aqueous alcohol in long flattened needles, m. p. 68—69° (Found: C, 68·2; H, 7·1. $C_{18}H_{23}O_2NS$ requires C, 68·1; H, 7·3%).

After removal of *p*-amino-*n*-amylbenzene from the product of rearrangement, a fraction was collected at 150—190°/16 mm., which consisted largely of a secondary amine. Repeated fractionation concentrated the secondary amine in the fraction 180—185°/16 mm. as a viscous liquid having the general properties and reactions of the alkylaminoalkylbenzenes. It was no doubt amylaminoamylbenzene, but no analysis was made, as it could not be freed from a small quantity of associated amines.

TABLE I.

						Products, g.				
Amine.	Wt., g.	Promoter.	Wt., g.	*t*.	Hours.	Unchanged amine.	NH_2Ph.	*p*-$NH_2{\cdot}C_6H_4R$.	*o*-$NH_2{\cdot}C_6H_4R$.	*p*-$NHR{\cdot}C_6H_4R$.
n-Amylaniline	5·90	$CoCl_2$	1·25	212°	13·0	2·82	0·91	2·52	—	0·60
	7·98		3·00	,,	16·75	1·38			—	2·93
n-Hexylaniline	5·76	$CoCl_2$	2·12	,,	13·46	1·07	0·40	2·68	—	2·19
	3·06		1·2	,,	14·37	0·65			—	1·85
	6·87		2·48	,,	23·66	1·23	0·82	1·83	—	2·10
n-Heptylaniline	6·92	$CoCl_2$	1·47	,,	17·80	not determined	0·57	1·40	—	3·20
	6·66		2·28		18·36	0·76			—	3·55
	6·64	$CoBr_2$	1·80	212	14·60	1·42	0·39	1·79	—	2·75
	6·38		2·97	,,	16·66	1·12	1·08	1·47	—	1·88
	5·77	$CoCl_2$	2·42	,,	20·66	0·79	0·52	1·61	—	1·78
n-Octylaniline	6·64	$CoCl_2$	1·72	,,	15·50	0·99	0·84	1·26	—	4·02
	6·50		1·81	,,	17·16	0·61			—	4·18
sec.-Octylaniline *	16·86	$CoBr_2$	6·36	,,	24·75	1·92	3·82	0·90		—
Dodecylaniline	9·72	$CoCl_2$	2·83	247	20·66	0·62	0·65	3·76	—	4·05
	8·12		2·6	212	23·5	0·77	0·69	1·75	—	4·49
Cetylaniline	6·38	$CoCl_2$	4·55	,,	20·55	0·54	not determined	1·23	—	3·20
	4·90		6·43		22	0·69	0·15	1·13	—	2·49
*cyclo*Hexylaniline †	21·2	$CoCl_2$	8·75	247	25·5	0·10	5·70	2·71	0·79	—
Benzylaniline ‡	15·3	$CoCl_2$	5·7	,,	15·8	0·38	1·50	4·05	0·83	0·21

* 4·91 G. of octene obtained, and 1·21 g. of a higher-boiling fraction (not further examined).

† 3·43 G. of *cyclo*hexene, 0·72 g. of a higher-boiling fraction, and a considerable amount of resin were also obtained.

‡ 4·2 G. of 2 : 4-dibenzylaniline isolated from the product.

Rearrangement of n-*Hexylaniline*.—*n*-Hexylaniline was prepared by heating aniline (100 g.) with *n*-hexyl iodide (50 g.) at 100°. After 6 hours, the product was made alkaline, and the bulk of the unchanged aniline removed by distillation. This recovered aniline (55 g.) together with an additional quantity (25 g.) was heated with a further amount of *n*-hexyl iodide (43 g.). The product was treated as described above, and the crude hexylaniline from both preparations combined. Repeated fractional distillation yielded n-*hexylaniline* (64 g.; 82%) as a colourless refractive liquid with a not very pleasant odour, b. p. 158°/28 mm. (Found: C, 81·3; H, 11·1; N, 7·8. $C_{12}H_{19}N$ requires C, 81·3; H, 10·8; N, 7·9%). It was further purified through its *hydrobromide*, which separated from concentrated alcoholic solution in large transparent tablets (Found: HBr, 31·2. $C_{12}H_{19}N,HBr$ requires HBr, 31·4%). The p-*toluenesulphonyl* derivative separated from alcohol in white well-shaped crystals, m. p. 67—68° (Found: C, 69·1; H, 8·1; N, 4·3. $C_{19}H_{25}O_2NS$ requires C, 68·9; H, 7·6; N, 4·2%), and the m-*nitrobenzenesulphonyl* derivative from aqueous alcohol in needles, m. p. 79—80° (Found: C, 59·4; H, 6·6. $C_{18}H_{22}O_4N_2S$ requires C, 59·7; H, 6·1%).

p-*Amino*-n-*hexylbenzene*, b. p. 146—148°/17 mm. (Found: C, 81·3; H, 11·1; N, 7·9. $C_{12}H_{19}N$ requires C, 81·3; H, 10·8; N, 7·9%), yielded a *hydrochloride* easily soluble in water and precipitated from aqueous solution by dilute hydrochloric acid (Found: HCl, 17·0. $C_{12}H_{19}N,HCl$ requires HCl, 17·1%). The *sulphate* was sparingly soluble in water [Found: H_2SO_4, 21·3. $(C_{12}H_{19}N)_2,H_2SO_4$ requires H_2SO_4, 21·7%]. The *acetyl* derivative crystallised from aqueous alcohol in platelets, m. p. 91° (Found: C, 76·8; H, 9·9; N, 6·5. $C_{14}H_{21}ON$ requires C, 76·7; H, 9·7; N, 6·4%).

p-n-*Hexylamino*-n-*hexylbenzene* was a slightly viscous, pale yellow liquid, b. p. 203—204°/18 mm. (Found: C, 83·2; H, 12·0. $C_{18}H_{31}N$ requires C, 82·7; H, 12·0%). Its *hydrochloride* crystallised from light petroleum (b. p. 40—60°) containing a little ethyl acetate (Found: C, 72·4; N, 4·8; Cl, 12·3. $C_{18}H_{31}N,HCl$ requires C, 72·6; N, 4·7; Cl, 11·9%).

Rearrangement of n-*Heptylaniline*.—The product obtained by heating a mixture of aniline (200 g.) and *n*-heptyl iodide (135 g.) at 100° for 6 hours was basified and distilled to remove the excess of aniline. Repeated fractionation of the residue furnished *n*-heptylaniline (73 g.) and crude di-*n*-heptylaniline (22 g.). A further purification of *n*-heptylaniline was effected through its hydrobromide. n-*Heptylaniline* was a liquid with a very faint straw-yellow tint, b. p. 160—161°/21 mm. (Found : C, 81·8; H, 11·4. $C_{13}H_{21}N$ requires C, 81·6; H, 11·1%). The *hydrobromide* was sparingly soluble in concentrated hydrobromic acid and easily soluble in alcohol; it crystallised well from alcohol–ether (Found : HBr, 29·8. $C_{13}H_{21}N,HBr$ requires HBr, 29·7%). The p-*toluenesulphonyl* derivative crystallised from alcohol in white prismatic needles, m. p. 76° (Found : C, 69·7; H, 8·0; N, 4·3. $C_{20}H_{27}O_2NS$ requires C, 69·5; H, 7·9; N, 4·1%), and the m-*nitrobenzenesulphonyl* derivative in silky needles, m. p. 96° (Found : C, 61·0; H, 6·5. $C_{19}H_{24}O_4N_2S$ requires C, 60·6; H, 6·4%).

p-*Amino*-n-*heptylbenzene* was a very pale yellow liquid, b. p. 159°/18 mm. (Found : C, 81·3; H, 10·8. $C_{13}H_{21}N$ requires C, 81·6; H, 11·1%). The *hydrochloride* crystallised from dilute hydrochloric acid in white needles (Found : HCl, 15·8. $C_{13}H_{21}N,HCl$ requires HCl, 16·0%). The *acetyl* derivative was obtained in white flattened needles, m. p. 91—92°, from aqueous alcohol (Found : C, 77·2; H, 10·1; N, 6·1. $C_{15}H_{23}ON$ requires C, 77·2; H, 9·9; N, 6·0%).

p-n-*Heptylamino*-n-*heptylbenzene* was a somewhat viscous oil with a pale straw-yellow tint, b. p. 220—223°/18 mm. (Found : C, 83·3; H, 12·3. $C_{20}H_{35}N$ requires C, 83·0; H, 12·2%). The addition of aqueous sodium nitrite to a solution of the amine in glacial acetic acid yielded a yellow oily nitrosoamine which gave a pronounced Liebermann nitroso-test. The addition of concentrated hydrochloric acid to an ethereal solution of the amine gave the *hydrochloride* as a white crystalline cake with a tinge of green; after drying in a vacuum over potash, this crystallised from light petroleum (b. p. 40—60°) in small white nodular aggregates, m. p. 83—85° (Found : C, 73·8; H, 11·3; N, 4·3. $C_{20}H_{35}N,HCl$ requires C, 73·7; H, 11·1; N, 4·3%). The hydrochloride was readily soluble in ether, benzene, chloroform, and alcohol, moderately soluble in light petroleum (b. p. 40—60°), and not easily soluble in hydrochloric acid.

The constitution of *p*-*n*-heptylamino-*n*-heptylbenzene was established by preparing it by refluxing *p*-amino-*n*-heptylbenzene (2·95 g.) and *n*-heptyl bromide (2·75 g.) for 24 hours in alcoholic solution containing suspended anhydrous sodium carbonate. The product, on fractionation, yielded *p*-*n*-heptylamino-*n*-heptylbenzene, b. p. 223°/18 mm., as a colourless oil, characterised by its hydrochloride, m. p. 83—85° after crystallisation from light petroleum (b. p. 40—60°), not depressed by the specimen described above.

Rearrangement of n-*Octylaniline*.—*n*-Octylaniline was prepared by the interaction of aniline (50 g.) and *n*-octyl iodide (25 g.) at 100° for 2 hours. The product was made alkaline, and the liberated amines fractionally distilled to separate the excess of aniline. After several distillations under reduced pressure, *n*-octylaniline was obtained as a colourless liquid (16 g.), b. p. 177—178°/25 mm. A small amount of a higher-boiling fraction was obtained and consisted presumably of di-*n*-octylaniline.

A second preparation from *n*-octyl bromide (23 g.) and aniline (50 g.) yielded 21 g. of *n*-octylaniline.

After a further purification through its hydrobromide, n-*octylaniline* was obtained as an almost colourless liquid, b. p. 177—178°/25 mm. (Found : C, 82·1; H, 11·4. $C_{14}H_{23}N$ requires C, 81·9; H, 11·3%). The p-*toluenesulphonyl* derivative crystallised from alcohol in fan-shaped clusters of needles, m. p. 42—43° (Found : N, 4·1. $C_{21}H_{29}O_2NS$ requires N, 3·9%).

p-Amino-*n*-octylbenzene was isolated as an almost colourless liquid, b. p. 170—172°/17 mm., which solidified on cooling; m. p. 19—21°. It was characterised by its acetyl derivative, m. p. 93—94°, benzoyl derivative, m. p. 115—116°, and p-*toluenesulphonyl* derivative, which formed needle-like crystals, m. p. 85—86°, from alcohol (Found : C, 70·4; H, 8·1; N, 4·3. $C_{21}H_{29}O_2NS$ requires C, 70·1; H, 8·1; N, 3·9%). Beran (*Ber.*, 1885, 18, 132) has described *p*-amino-*n*-octylbenzene, m. p. 19·5°, the acetyl derivative, m. p. 93°, and the benzoyl derivative, m. p. 117°.

p-n-*Octylamino*-n-*octylbenzene* distilled as a viscous, pale yellow liquid, b. p. 232—235°/14 mm., which solidified on cooling; m. p. 11—13° (Found : C, 83·3; H, 11·9. $C_{22}H_{39}N$ requires C, 83·3; H, 12·3%).

Rearrangement of sec.-*Octylaniline*.—*sec*.-Octylaniline was prepared from *sec*.-octyl bromide (50 g.) and aniline (100 g.) following the procedure described in the preceding preparations (compare J., 1935, 1282).

Anhydrous cobalt bromide (6·36 g.) and *sec*.-octylaniline (16·86 g.) were heated together at 212° for 24·75 hours in a wide vertical tube closed at the lower end; the upper end was attached to a downward condenser. Octene, b. p. 123—125°, distilled from the mixture and the last traces were removed by a gentle stream of carbon dioxide (yield, 4·97 g.). The non-volatile product yielded aniline (4·02 g.), unchanged *sec*.-octylaniline (1·92 g.), amino-*sec*.-octylbenzene (0·9 g.),

b. p. 165—170°/26 mm., and a fraction (1·21 g.), b. p. 180—230°/25 mm., from which a pure compound could not be isolated.

The amino-*sec*.-octylbenzene proved to be a mixture, for on acetylation it gave a slowly crystallising oil, from which p-*acetamido*-sec.-*octylbenzene* was isolated by fractionation, m. p. 84—85° (Found: C, 77·8; H, 10·4. $C_{16}H_{25}ON$ requires C, 77·7; H, 10·2%). Hydrolysis of this acetyl compound and benzoylation of the resulting amine yielded *p*-benzamido-*sec*.-octylbenzene, m. p. 107—109°, identical with that prepared by Beran's method (*loc. cit.*). The more soluble fractions from the purification of *p*-acetamido-*sec*.-octylbenzene were of lower m. p. and gave analytical figures approximating to those for acetamido-*sec*.-octylbenzene (Found: C, 77·8, 77·3; H, 10·5, 10·5%). It is evident that in this rearrangement a mixture of at least two isomeric amino-octylbenzenes is formed.

Rearrangement of Dodecylaniline.—*Dodecylaniline* was obtained by heating together aniline (50 g.) and dodecyl iodide (34 g.) at 120° for 3½ hours. Distillation of the product after basification yielded dodecylaniline, b. p. 212—214°/13 mm. (yield, 24·6 g.; 82%), and a residue (3·0 g.), presumably of didodecylaniline, distilling chiefly at 280—295°/12 mm. The former crystallised from methyl alcohol in needles, m. p. 27—28° (Found: C, 83·0; H, 12·2. $C_{18}H_{31}N$ requires C, 82·7; H, 12·0%). The *hydrochloride*, obtained by addition of concentrated hydrochloric acid to an ethereal solution of the amine, crystallised well from acetone or ethyl acetate; m. p. 88—91°. For analysis it was obtained from benzene–light petroleum in glistening scales (Found: C, 72·8; N, 4·6. $C_{18}H_{31}N,HCl$ requires C, 72·6; N, 4·7%). The p-*toluenesulphonyl* derivative crystallised from methyl alcohol in thin plates, m. p. 53—54° (Found: N, 3·5. $C_{25}H_{37}O_2NS$ requires N, 3·4%).

Rearrangement of dodecylaniline was effected by heating at 247° with anhydrous cobalt chloride. The product, after being freed from cobalt chloride, was distilled, yielding aniline as the first fraction and a mixture of p-*aminododecylbenzene* and dodecylaniline at 200—216°/13 mm. The residue (*A*) consisted of p-*dodecylaminododecylbenzene*.

p-Aminododecylbenzene was freed from associated dodecylaniline by treatment with dilute sulphuric acid and ether; it was recovered from the sparingly soluble sulphate and purified through its acetyl derivative. The ethereal and aqueous solutions from the separation of the sulphate of the primary amine yielded dodecylaniline on basification. *p*-Aminododecylbenzene crystallised from methyl alcohol in fan-shaped clusters of needles, m. p. 41—42° (Found: C, 83·0; H, 12·0. $C_{18}H_{31}N$ requires C, 82·7; H, 12·0%). p-*Acetamidododecylbenzene* separated from aqueous alcohol in nacreous platelets, m. p. 101—101·5° (Found: C, 79·3; H, 11·0; N, 4·6. $C_{20}H_{33}ON$ requires C, 79·1; H, 11·0; N, 4·6%).

p-Dodecylaminododecylbenzene was isolated by extraction of the residue (*A*) with boiling methyl alcohol; a small amount of dark resinous matter remained. *p*-Dodecylaminododecylbenzene separated from the methyl-alcoholic extract and a further amount was obtained by concentration of the filtrate. The product, after crystallisation, was obtained in small white clusters of needles, m. p. 48—49° (Found: C, 83·8; H, 12·8. $C_{30}H_{55}N$ requires C, 83·8; H, 12·9%). The identity of this compound was established by its preparation from *p*-aminododecylbenzene and dodecyl iodide. These two were heated together for 30 hours in alcoholic solution containing anhydrous sodium carbonate in suspension. After removal of the solvent and inorganic matter, the residue was crystallised from acetone; it had m. p. 48—49°, not depressed by the above specimen. A comparison of the hydrochlorides and nitrosoamines (mixed m. p., appearance) from both specimens further established the identity.

The *hydrochloride* was precipitated by the addition of concentrated hydrochloric acid to an ethereal solution of the amine. After drying, it separated from ethyl acetate as a white crystalline powder, m. p. 84—85° with previous softening from 82° (Found: C, 77·3; N, 3·2. $C_{30}H_{55}N,HCl$ requires C, 77·3; N, 3·0%). The *nitrosoamine* was precipitated as a yellowish oil by the addition of a solution of sodium nitrite in acetic acid containing a little water to a solution of the amine in glacial acetic acid. It solidified on cooling, and after being washed with water and crystallised from acetone formed very thin, narrow platelets, m. p. 40—41° (Found: C, 78·6; H, 12·0. $C_{30}H_{54}ON_2$ requires C, 78·5; H, 11·9%).

Rearrangement of Cetylaniline.—The cetylaniline was prepared by heating together cetyl iodide (50 g.) and aniline (30 g.) in a boiling water-bath for 3 hours. Distillation of the basified product yielded unchanged aniline, a small intermediate fraction, b. p. 180—240°/24 mm., and the main fraction, b. p. 255—285°/23 mm. (yield, 21·38 g.), consisting essentially of cetylaniline. A residue boiling above 285°/23 mm. was largely dicetylaniline. The pure cetylaniline boiled at 265—267°/23 mm. and solidified on cooling. It separated from methyl alcohol in long needles which slowly changed to aggregates of small needles, m. p. 41—43° (Fridau, *Annalen*, 1852,

83, 29, gives m. p. 42°). It was characterised by its *nitrosoamine*, which, prepared in the usual way, crystallised from methyl alcohol in pale yellow clusters of small needles, m. p. 40—41° (Found: C, 76·3; H, 11·0; N, 7·9. $C_{22}H_{38}ON_2$ requires C, 76·2; H, 11·1; N, 8·1%), easily soluble in light petroleum, ethyl acetate, chloroform or benzene, not readily so in cold ethyl or methyl alcohol. The p-*toluenesulphonyl* derivative crystallised from alcohol in very thin platelets, m. p. 64—65° (Found: C, 73·7; H, 10·0; N, 3·0. $C_{29}H_{45}O_2NS$ requires C, 73·8; H, 9·6; N, 3·0%).

The experimental procedure for the rearrangement of cetylaniline and the isolation of the products closely followed that described for dodecylaniline. Cetylaniline (6·38 g.) and anhydrous cobalt chloride (4·55 g.), heated together at 212° for 20·55 hours, gave a product which was separated by distillation into aniline, a fraction, b. p. 200—270°/26 mm. (1·83 g.), and a dark residue (*B*) (3·20 g.). The fraction, b. p. 200—270°/26 mm., was resolved by treatment with dilute sulphuric acid and ether into *p*-aminocetylbenzene (1·23 g.) and cetylaniline (0·54 g.).

p-Aminocetylbenzene crystallised from methyl alcohol in small needles, m. p. 51—52°, and formed an acetyl derivative, m. p. 102·5—103·5° (Found: C, 80·0; H, 11·5. Calc. for $C_{24}H_{41}ON$: C, 80·15; H, 11·5%). The p-*nitrobenzylidene* derivative crystallised from acetic acid as a yellow felted mass of needles, m. p. 71° (Found: N, 6·1. $C_{29}H_{42}O_2N_2$ requires N, 6·2%). For comparison, *p*-aminocetylbenzene was prepared by the reaction of cetyl alcohol, aniline, and zinc chloride. The main product was identical with that obtained in the rearrangement of cetylaniline, as shown by comparison (mixed m. p., appearance, and qualitative solubilities) of the free amines and the acetyl and the *p*-nitrobenzylidene derivatives.

The dark residue (*B*) was extracted repeatedly with boiling alcohol, leaving a small black residue. The extract deposited 2·15 g. of crystalline material, which after crystallisation from acetone and benzene was obtained as white bulky aggregates of needles, m. p. 62—63° (Found: C, 84·6, 84·8; H, 13·5, 12·9. $C_{38}H_{71}N$ requires C, 84·2; H, 13·2%). It was identified as p-*cetylaminocetylbenzene* by comparison (mixed m. p.) with a specimen prepared by heating cetyl iodide (3·5 g.), *p*-aminocetylbenzene (3·0 g.), and an excess of anhydrous sodium carbonate in absolute alcohol (20 c.c.) for 20 hours.

p-*Cetylphenylcetylnitrosoamine*, prepared by adding a solution of nitrous acid in glacial acetic acid to a solution of the amine in the same solvent, separated as a bulky yellow precipitate, which was purified by extraction with boiling light petroleum and crystallisation of the extract from acetone. It formed buff-coloured aggregates, m. p. 55° (Found: C, 80·1; H, 12·5. $C_{38}H_{70}ON_2$ requires C, 79·9; H, 12·4%), and gave a greenish-blue coloration when warmed with concentrated sulphuric acid and phenol.

Rearrangement of cyclo*Hexylaniline*.—Heating with anhydrous cobalt chloride at 212° was unsatisfactory, the greater part of the secondary amine being recovered after 17½ hours' heating; there was, however, a strong odour of *cyclo*hexane. Rearrangement at 247° gave better results. *cyclo*Hexylaniline (21·2 g.) and anhydrous cobalt chloride (8·75 g.) were heated together at 247° for 25½ hours in an apparatus similar to that used for the rearrangement of *sec.*-octylaniline. A distillate began to collect after 5—6 hours' heating and most of it was collected within 8 hours of the commencement of the heating. It amounted to 3·43 g., had b. p. 81—82°, was unsaturated, and had the characteristics of *cyclo*hexene. The product remaining in the decomposition tube, after basification and distillation, gave aniline (5·70 g.), a fraction, b. p. 140—175°/20 mm. (3·60 g.), a fraction, b. p. 175—235°/20 mm. (0·72 g.), and a thick residual varnish.

The fraction, b. p. 140—175°/20 mm., was resolved into *p*-amino*cyclo*hexylbenzene (2·71 g.), m. p. 46—48° (crude), *o*-amino*cyclo*hexylbenzene (0·7 g.), and *cyclo*hexylaniline (0·10 g.) (see J., 1932, 2648). The higher-boiling fraction (175—235°/20 mm.) contained a considerable proportion of a primary amine, but it has not yet been possible to isolate any pure product from it.

Rearrangement of Benzylaniline.—Anhydrous cobalt chloride (5·7 g.) and benzylaniline (15·3 g.) were heated together at 247° for 15·8 hours, a basic vapour being evolved. After the usual treatment the product yielded aniline (1·5 g.), a fraction (*C*), b. p. 110—200°/13 mm. (5·26 g.), a fraction (*D*), b. p. 200—260°/13 mm. (4·63 g.), and a dark resin-like mass of higher b. p. (3·27 g.).

The fraction (*C*), the greater part of which boiled at 180—185°/13 mm., was resolved, by treatment with dilute sulphuric acid, into unchanged benzylaniline (0·38 g.) and a mixture of *p*-aminodiphenylmethane and an isomeric primary amine which is provisionally assumed to be *o*-aminodiphenylmethane. These were separated by means of aqueous zinc chloride, which precipitated the bulk of the *p*-amine as a sparingly soluble zincichloride. The *o*-amine reacted only slightly.

p-Aminodiphenylmethane was purified through its acetyl derivative, which formed scales, m. p. 128°, from benzene and yielded the pure *p*-amine, m. p. 36—37°, on hydrolysis (Basler, *Ber.*, 1883, **16**, 2718, gives m. p. 34—35°). This amine was further characterised by its p-*nitrobenzylidene* derivative, golden-yellow flat needles from alcohol, m. p. 101—102° (Found : C, 76·0; H, 5·1; N, 8·9. $C_{20}H_{16}O_2N_2$ requires C, 75·9; H, 5·1; N, 8·9%), and by its *condensation product* with 2 : 4-dinitrochlorobenzene, brick red needles, m. p. 128—129° (Found : C, 65·1; H, 4·4; N, 12·4. $C_{19}H_{15}O_4N_3$ requires C, 65·3; H, 4·3; N, 12·0%). Reaction of the amine in light petroleum with phenylthiocarbimide gave p-*benzyl*-αβ-*diphenylthiourea*, which formed a crystalline powder from acetic acid, m. p. 148—149° (Found : C, 75·3; H, 6·1; N, 9·1. $C_{20}H_{18}N_2S$ requires C, 75·4; H, 5·7; N, 8·8%).

The crude *o*-aminodiphenylmethane on acetylation gave a product which after several crystallisations from alcohol and acetic acid melted at 126° (Found : C, 80·2; H, 6·6. Calc. : C, 80·0; H, 6·7%) (Carré, *Bull. Soc. chim.*, 1909, **5**, 121, describes *o*-acetamidodiphenylmethane, m. p. 135°). It strongly depressed the m. p. of the corresponding *p*-compound.

The fraction (*D*), b. p. 250—260°/13 mm., contained an appreciable proportion of a primary amine. This was precipitated as sulphate by the addition of a slight excess of dilute sulphuric acid, recovered, and converted into an *acetyl* derivative, which formed felted needles, m. p. 145—146°, from alcohol (Found : C, 83·9; H, 6·2; N, 4·4. $C_{22}H_{21}ON$ requires C, 83·8; H, 6·7; N, 4·4%). Hydrolysis of the acetyl derivative furnished pure 2 : 4-*dibenzylaniline*, which crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 49—50° (Found : C, 88·2; H, 7·0; N, 5·2. $C_{20}H_{19}N$ requires C, 87·9; H, 7·0; N, 5·1%).

The filtrate from the precipitation of the sulphate was acidified more strongly and treated with sodium nitrite. A nitrosoamine (0·25 g.), presumably derived from benzylaminodiphenylmethane, was obtained, but nothing was isolated from it in a satisfactory state for analysis. After removal of the nitrosoamine, the aqueous acid solution was warmed till all diazo-compounds were decomposed and then made strongly alkaline; a tertiary amine (less than 0·02 g.) was liberated. The free amine was white; an aqueous solution of its hydrochloride had a strong yellow colour with a green fluorescence. It gave a white mercurichloride, m. p. 190—193° after softening from 185°. The amount available did not permit of further crystallisation or of mixed m. p. determinations (acridine mercurichloride has m. p. 234° and phenanthridine mercurichloride, m. p. 197°).

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