85. *Rearrangement of the Alkylanilines. Part VII. The Behaviour of Alkylanilines with* tert.*-Alkyl Groups.*

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In earlier papers (J., 1931, 1281; 1932, 2396) evidence was adduced to support the view that, if hydrogen halides are used as promoters, the rearrangement of alkylanilines containing alkyl groups higher than propyl is due largely to the elimination of the alkyl group as olefin. Subsequent reaction of the olefin with the aromatic nucleus furnishes the so-called rearrangement product.

A detailed examination of the reaction of olefins with arylamines has shown that the products are of two types, (1) a secondary amine, resulting from the saturation of the olefinic linkage by the amino-group, and (2) an aminoalkylbenzene, which has been considered to be formed by combination of the olefin with the aromatic nucleus (J., 1932, 2646; 1934, 319, 1981; 1935, 1279). The following table summarises some of the results obtained, and it is clear that, under conditions comparable with those obtaining in the rearrangement, the yields of secondary amine are small; only under specially favourable conditions, notably the use of an excess of arylamine, can any appreciable amount of secondary amine be obtained. Octene is the only exception to these generalisations, and it will be referred to in a subsequent paper.

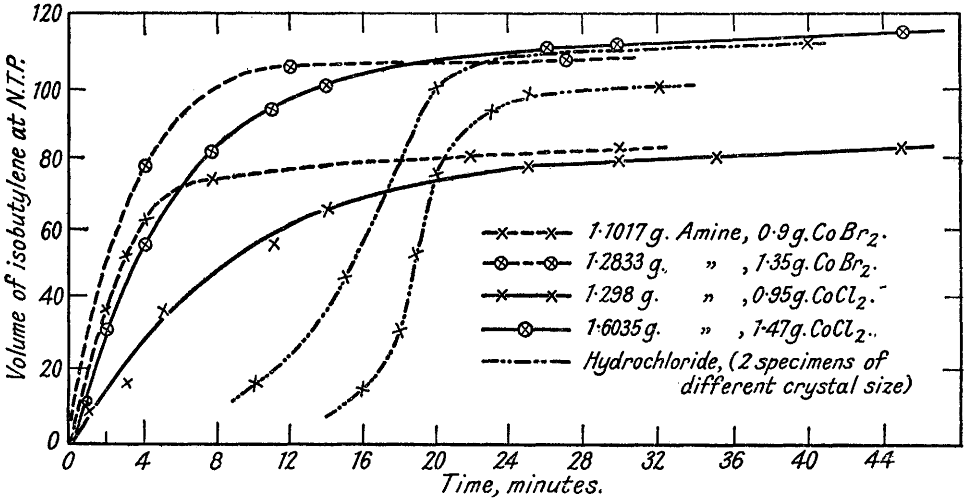
In an earlier communication the deduction was made, from a number of considerations, that the aminoalkylbenzene is produced by the direct reaction of the olefin with the nucleus of the aromatic amine rather than by rearrangement of the secondary amine. Support for this view is afforded by the known difficulty of forming a secondary amine by saturating the double bond of an olefinic hydrocarbon by an amino-group. Indeed, except for the examples referred to in the table, no other authentic examples of such a reaction are known to the author.

Aniline,							Yield of amine, g.	
g.	Promoter.	G.	Olefin.	G.	Temp.	Hours.	Secondary.	Primary.
80	NH_2,Ph,HCl	10	$CMe_2{:}CH_2$	5	220—240°	22	0·61	1·45
30	NH_2Ph,HBr	1	$CMe_2{:}CHMe$	6	230—250	6	0·51	1·80
30	NH_2Ph,HBr	3	,, ,,	6	230—250	6·5	0·57	3·7
40	NH_2Ph,HBr	4	,, ,,	7·1	240—260	5·5	1·84	3·3
100	NH_2Ph,HCl	6	,, ,,	12	240—260	25	0·59	6·85
100	$(NH_2Ph)_2,CoCl_2$	8	,, ,,	14·5	245	24	0·37	2·71
50	NH_2Ph,HCl	4	$CMeEt{:}CHMe$	10·5	230—270	5	1·7	2·7
6	NH_2Ph,HCl	3	,, ,,	3·5	285—290	3·5	trace	1·02
50	NH_2Ph,HCl	8	$CEt_2{:}CHMe$	10	230—260	12	0·35	1·22
5	NH_2Ph,HCl	2	$CHPh{:}CH_2$	5	270	6	trace	3·50
40	NH_2Ph,HCl	8	,, ,,	10·8	200—240	6	0·68	5·26
50	$(NH_2Ph)_2,CdCl_2$	7·7	,, ,,	7·2	235	24	0·09	0·94
50	$(NH_2Ph)_2,CoCl_2$	5·6	,, ,,	9·1	240	24	0·3	0·69
7·2	NH_2Ph,HBr	13·3	$C_{10}H_{10}$*	9·9	220	6	nil	9·8
40	NH_2Ph,HCl	12	Δ^{α}- and Δ^{β}-Octenes	7·2	210—240	24	1·0	0·1

* Dihydronaphthalene.

In order to submit these views to further investigation, particularly to ascertain if any serious amount of primary amine could be formed from the secondary by rearrangement under the conditions employed, some of the alkylanilines produced by the addition of aniline to olefins have been heated with cobalt halides or as their hydrogen halide salts, under conditions which normally bring about rearrangement (Hickinbottom, J., 1927, 64; 1932, 2398; Hickinbottom and Preston, J., 1930, 1569), in such a way that the olefin formed could be easily removed from the reaction mixture before undesirable secondary reactions could take place. This condition restricted the choice of suitable secondary amines to those which could yield a readily volatile olefin. For this reason, most of the experimental work was carried out with *tert.*-butylaniline, which has the advantage of permitting a simple and rapid measurement of the rate of decomposition.

When *tert.*-butylaniline is heated at 212° with anhydrous cobalt chloride or bromide, aniline is formed owing to the elimination of the *tert.*-butyl group as *iso*butylene. The rate of evolution depends, *ceteris paribus*, on the concentration of the metal halide. This is shown in the figure, which records the volume of *iso*butylene at N.T.P. evolved from 1 g. of base with various amounts of catalyst. The product left after heating consisted largely of aniline and the cobalt halide with some unchanged secondary amine. The amount of *p*-amino-*tert*.-butylbenzene isolated was 0·7 % of the weight of aniline present. The approximate accuracy of this assay was confirmed by analyses of the primary amines from two other decompositions, the results of which gave 1·7 % of *p*-amino-*tert*.-butylbenzene in the product. With *tert*.-hexylaniline, similar results were obtained by heating with cobalt halides : a rapid evolution of γ-methyl-Δ^{β}-pentene and the formation of aniline. Although it was not possible to isolate any rearrangement product owing to the relatively small amount of starting material, analyses of the primary amine from two decompositions gave 3·7 and 1·7 % of rearrangement product. The decomposition of *tert*.-butylaniline hydrochloride at 212° followed the same course as with cobalt halides, namely, the rapid evolution of *iso*butylene.



It is clear that both *tert*.-butylaniline and *tert*.-hexylaniline suffer extensive decomposition when heated with cobalt halides or as hydrochloride, and the amount of rearrangement is quite insufficient to account for the yields of *p*-amino-*tert*.-butyl- or -hexyl-benzene obtained by reaction of *iso*butylene or γ-methyl-Δ^{β}-pentene with aniline. This is held to afford support for the view already expressed that the formation of aminoalkylbenzenes from olefins is due to the direct reaction of the olefin with the aromatic nucleus.

EXPERIMENTAL.

Thermal Decomposition of tert.-*Butylaniline*.—(a) *With metal salts*. *tert*.-Butylaniline (7 g.) and anhydrous cobalt chloride (3·5 g.) were heated together at 212° for 45 minutes in a long narrow tube with a bulb blown at the lower end. During the first 10 minutes there was a vigorous evolution of gas; thereafter the tube contained a considerable amount of dark blue solid. The gas was collected in chloroform, cooled in ice, to which a concentrated solution of bromine in chloroform was added gradually so that it remained faintly coloured. After ¾ hour the chloroform solution was distilled, giving a small fraction, b. p. *ca*. 90°, and a main fraction, b. p. 146—149°, consisting of *iso*butylene dibromide. The dark blue solid, on decomposition with ammonia, yielded a mixture, which was separated into primary and secondary amines by treatment with aqueous zinc chloride. The primary amine consisted largely of aniline (b. p. and acetyl derivative), and a small residue of somewhat higher b. p. remained. From this, by conversion into acetyl derivative and subsequent crystallisation, 0·022 g. of *p*-acetamido-*tert*.-butylbenzene (m. p. 160—164°) was isolated, which, after further purification, was identified by m. p. and mixed m. p. This corresponds to a yield of 0·017 g. of *p*-amino-*tert*.-butylbenzene. The yield of aniline was 2·49 g. The secondary amine consisted of unchanged *tert*.-butylaniline (1·51 g.).

The volume of butylene evolved in this decomposition was determined by attaching the top of the reaction tube to an azotometer. When the heating had been continued for the requisite period, the apparatus was swept out by a current of carbon dioxide. The *iso*butylene was then determined by absorption in bromine water. The results are summarised below.

Butylaniline, g.	Metal salt, g.		Duration of heating, mins.	Vol. of butylene, c.c.	Yield of butylene, %.
1·0077	$CoCl_2$	0·7	30	92·8	61·7
1·1017	$CoBr_2$	0·9	30	82·3	54·8
1·2833	$CoBr_2$	1·35	30	107·5	71·6
1·2980	$CoCl_2$	0·95	55	91·1	60·7

The rearrangement of *tert.*-butylaniline (8·45 g.) and anhydrous cobalt chloride (3·4 g.) at 212° for 13 hours gave 3·97 g. of aniline and 0·08 g. of crude *p*-acetamido-*tert.*-butylbenzene (m. p. 160—163°). The yield of rearrangement product is 1·6% of the weight of aniline formed.

No increase in the proportion of rearrangement product was observed if the temperature was raised. In one such experiment, *tert.*-butylaniline (8·88 g.) and cobalt chloride (3·60 g.) were heated at 237°. After 20 hours there was a slight evolution of ammonia owing to the formation of some diphenylamine. The reaction was therefore stopped at this stage. The product consisted of aniline, 4·99 g.; diphenylamine, 0·05 g.; other secondary and tertiary amines, 0·16 g.; *p*-amino-*tert.*-butylbenzene, 0·02 g. The yield of rearrangement product is 0·45% of the weight of aniline formed.

(b) *Decomposition of* tert.*-butylaniline hydrochloride.* The heating was effected under conditions similar to those described above. On heating at 212° the crystals decrepitate, then gradually soften, and an effervescence sets in with a steady evolution of a gas which was identified as *iso*butylene.

After 30—60 mins.' heating, the residue was found to consist of aniline hydrochloride with some unchanged *tert.*-butylaniline hydrochloride. It was not possible to detect with certainty the presence of *p*-amino-*tert.*-butylbenzene; if it is formed, the amount must be very small. The results are summarised below, the rate of evolution of butylene being recorded in the figure.

				Loss of HCl during heating,	
Butylaniline hydrochloride, g.	Heating at 212°, mins.	Vol. of butylene at N.T.P., c.c.	Yield of butylene, %.	g.	as % of butyl group evolved as C_4H_9Cl.
0·7563	60	not determined		0·0029	2·0
0·3754	45	30·4	67·1	—	—
0·4802	32	37·0	63·7	0·0036	3·1
0·8667	45	79·1	75·6	not determined	

Thermal Decomposition of tert.*-Hexylaniline.*—*tert.*-Hexylaniline (3·74 g.) and anhydrous cobalt bromide (4 g.) were heated at 212° for 2 hours. After about ½ hour the metal bromide had swollen so that the contents of the tube appeared free from liquid. The volatile product (1·33 g.), b. p. 67—68°, had all the characteristics of an olefin (γ-methyl-Δ^{β}-pentene boils at 68°). The residue after the reaction gave 0·05 g. of unchanged secondary amine. The primary amine consisted essentially of aniline (b. p. and acetyl derivative). The amount of rearrangement product was determined by evaporating the primary amine with hydrochloric acid and drying the residue to constant weight. Determination of the hydrogen chloride in the dry salt gave HCl, 27·74%, which is equivalent to 3·7% of *p*-amino-*tert.*-hexylbenzene.

In a further experiment, 3·37 g. of *tert.*-hexylaniline and 4 g. of anhydrous cobalt chloride, heated together for 2½ hours at 212°, gave 0·25 g. of unchanged secondary amine, and a primary amine which consisted almost entirely of aniline. Analysis of the dried hydrochloride of the primary amine gave HCl, 27·93%, corresponding to 1·6% of *p*-amino-*tert.*-hexylbenzene.

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