255. *The Elimination of Tertiary Alkyl Groups from Alkylanilines by Hydrolysis.*

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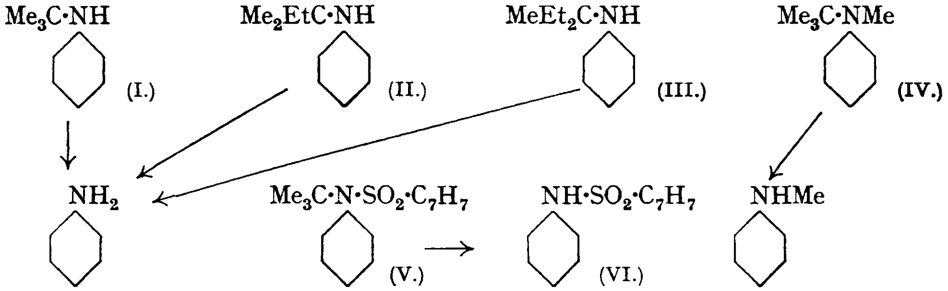
It has been shown (this vol., p. 946) that those alkylanilines with *tert.*-alkyl groups have some unusual reactions, but the most striking is the elimination of this group under the influence of warm aqueous mineral acid. Each of the amines examined in the present investigation, *viz.*, *tert.*-butyl- (I), amyl- (II), and hexyl-aniline (III), yields aniline when heated with 15*N*-sulphuric acid at 110—140°. Concentrated hydrobromic and hydriodic acids and moderately concentrated phosphoric acid have been found to have a similar action on *tert.*-butylaniline. The experimental results are summarised below.

		Acid.		Heated		Yield, g.	
Amine.	Wt., g.	Concn.	Vol., c.c.	for (hrs.)	at	Aniline.	Unchanged amine.
tert.-Butylaniline	2·60	15*N*-H_2SO_4	20	14·2	120—140°	0·74	0·87
,, ...	2·68	19*N*-H_2SO_4	15	8·5	135—145	0·49	1·57
,, ...	0·72	Aq. HBr, *d* 1·49	3	12·5	124—145	0·07	0·48
,, ...	2·73	Aq. HI, *d* 1·7	15	5	130	0·5	0·87
,, ...	0·98	70% H_3PO_4	15	14·5	140	0·3	0·29
tert.-Amylaniline	1·12	19*N*-H_2SO_4	5	11	110—120	0·08	
,, ...	0·77	19*N*-H_2SO_4	·6	14·3	125—130	0·25	0·17
tert.-Hexylaniline	0·75	19*N*-H_2SO_4	4	1	125—130	0·13	
,, ...	1·68	15*N*-H_2SO_4	10·5	6	120—130	0·65	0·65
,, ...	3·05	15*N*-H_2SO_4	14	10	110—120	0·92	

It is generally assumed that the alkyl groups of the alkylanilines are stable to hot aqueous mineral acids, and this is supported by the fact that, whereas many acyl- and aryl-sulphonyl derivatives of the alkylanilines have been hydrolysed by mineral acids, yet there is no record of the alkyl groups being split off during this operation, although this would certainly occur if the alkyl group were sensitive to acid hydrolysis. Further, determinations of the behaviour of methyl- and ethyl-anilines towards concentrated hydriodic acid under Zeisel's conditions have shown that none of the ethyl groups is split off after 5 hours, while only 3·4% of the methylaniline yields methyl iodide (Goldschmiedt, *Monatsh.*, 1906, **27**, 849; 1907, **28**, 1063). A more exact comparison was instituted by heating *n*-butylaniline with 19*N*-sulphuric acid at 120—140°. After 30 hours' heating, no primary amine could be detected, and at least 80% of the secondary amine was recovered as its pure *p*-toluenesulphonyl derivative. Further information on the relative stability of the tertiary alkyl groups was obtained by heating methyl-*tert.*-butylaniline (IV) with 19*N*-sulphuric acid. The tertiary butyl group was split off, and methylaniline obtained; no aniline could be detected in the product.

There can be, therefore, no reasonable doubt that the tertiary alkyl group in alkylanilines is unusually sensitive to hot mineral acids and is eliminated under conditions which do not affect other alkylanilines. A confirmation of this is provided by the behaviour of the *p*-toluenesulphonyl derivative of *tert.*-butylaniline (V). When it is heated with 15*N*-sulphuric acid, at least 85% of the *tert.*-butyl group is eliminated in an hour, *p*-toluenesulphonanilide being formed. The *m*-nitrobenzenesulphonyl derivative behaves similarly.

Attempts were made to eliminate the tertiary alkyl group from phenyl-*tert.*-butylnitrosoamine by the action of sulphuric acid and so obtain a diazo-compound. The reaction was complicated by the elimination of the nitroso-group under the conditions employed, but there was evidence of the formation of a small yield of diazo-compound. It is of interest that the characteristic colour changes associated with the Liebermann reaction could be obtained when the nitrosoamine was treated with sulphuric acid under suitable conditions without the addition of phenol.



It was hoped to examine the stability of the nitrated derivatives of *tert.*-butylaniline towards acid hydrolysis. According to the usual views of the effect of the nitro-group, they should more readily lose the alkyl group by hydrolysis than the unsubstituted amine. It has not yet been possible to test this directly owing to difficulties encountered in the nitration of *tert.*-butylaniline and to lack of material. It is, however, possible to obtain evidence on this point from the observations of Morgan and Hickinbottom (*J. Soc. Chem. Ind.*, 1924, **43**, 307T), who found that di- and tetra-nitrodi-*p*-tolylaminobutanes fairly easily yielded nitrotoluidines by the action of hot dilute sulphuric acid, whilst βγ-di-*p*-tolylaminobutane is not decomposed under these conditions (compare Morgan, Hickinbottom, and Barker, *Proc. Roy. Soc.*, *A*, 1926, **110**, 518, footnote).

EXPERIMENTAL.

Action of Aqueous Mineral Acids on Alkylanilines with tert.*-Alkyl Groups.*—A weighed quantity of the amine was heated under reflux with a known amount of the acid specified in the above table. When sulphuric acid was used, the elimination of the alkyl group was accompanied by a production of carbonaceous matter and the gradual evolution of sulphur dioxide. With phosphoric acid, there was scarcely any darkening, and the solution finally had a strong odour of *tert.*-butyl alcohol.

After a definite period of heating, the solution was cooled, diluted, filtered (this was only necessary with sulphuric acid, see above), and made up to a known volume; an aliquot portion was then tested for the presence of aniline by diazotisation. The remainder of the solution was rendered alkaline with a slight excess of ammonia, extracted several times with ether, the extract dried (potassium carbonate), and the solvent removed at as low a temperature as possible. The residual amines were suspended in water, and acetic anhydride was added in small quantities till its odour persisted after 2 or 3 minutes. The mixture was then kept for some hours, treated with a slight excess of very dilute hydrochloric acid, and extracted several times with ether. The ethereal solution thus obtained was washed twice with very dilute hydrochloric acid, then with water, and finally dried (magnesium sulphate). Evaporation of the solvent left acetanilide, usually contaminated with a trace of the acetyl derivative of the secondary amine. It was purified by dissolving it in hot water, and evaporating the filtered solution. The weight of acetanilide thus obtained was used to calculate the yield of aniline recorded in the table. The purity of the product from each hydrolysis was checked by m. p. (112—114°) and mixed m. p. A number of specimens from several experiments were mixed and analysed (Found: C, 71·4; H, 6·6. Calc.: C, 71·1; H, 6·7%).

The aqueous acid solutions remaining after ether extraction of acetanilide yielded the unchanged secondary amines on addition of excess of aqueous alkali. In experiments with *tert.*-butyl- and -amyl-aniline, the identity of the secondary amine was determined by conversion into the corresponding nitrosoamine. *tert.*-Hexylaniline was identified by its picrate (this vol., p. 950). The results, for which no high order of accuracy is claimed, are summarised in the table. The yields of aniline and secondary amine are calculated from the weights of pure substances or their derivatives which have been isolated; they represent, therefore, minimum amounts present in the mixture.

For comparison, *n*-butylaniline (1·42 g.) was heated with 10 c.c. of 19*N*-sulphuric acid at 120—135° (chiefly at 130—135°). After 30 hours' heating, the solution was diluted to 50 c.c., whereupon 1 c.c. gave no test for a primary amine on treatment with nitrous acid and alkaline R-salt. After addition of excess of alkali and then *p*-toluenesulphonyl chloride in ether to the remainder, the *p*-toluenesulphonyl derivative of *n*-butylaniline was obtained (2·27 g., m. p. 52—54°), corresponding to 80% of the theoretical amount. A trace of a product (0·01 g.) soluble in aqueous alkali was formed, but it could not be crystallised.

*Action of Aqueous Sulphuric Acid on Methyl-*tert.*-butylaniline.*—The base (0·64 g.) was heated with 2 c.c. of 19*N*-acid for 13 hours at 120—140° (chiefly at 130—140°). A dark solution with a strong odour of sulphur dioxide was obtained. It was diluted to 25 c.c., and 1 c.c. gave a strong test for a secondary amine. The amine was liberated from a portion of the remainder (an undetermined amount was lost accidentally) and *p*-toluenesulphonated. *p*-Toluenesulphonmethylanilide (0·35 g.), m. p. 92—93°, was obtained. The m. p. was raised to 94° by two crystallisations from alcohol, and was not depressed by admixture with an authentic specimen. A trace (0·01 g.) of a *p*-toluenesulphonyl derivative soluble in aqueous alkali was also obtained; unchanged methyl-*tert.*-butylaniline amounted to 0·015 g.

Action of Aqueous Sulphuric Acid on p-*Toluenesulphon*-tert.-*butylanilide* (V): *Formation of* p-*Toluenesulphonanilide.*—The *p*-toluenesulphonyl derivative (V) (0·60 g.) was heated with 4 c.c. of 15*N*-sulphuric acid at 135—145°. There was a brisk frothing during the first 20 mins. After 1 hour, the product consisted of an almost colourless lower acid layer covered with a brownish viscous oil. It was diluted with water, the oil taken up in ether, and the extract shaken several times with dilute aqueous alkali. Evaporation of the ethereal solution left 0·01 g. of unchanged *p*-toluenesulphonyl derivative. Acidification of the alkaline extracts furnished 0·41 g. of crystalline solid, m. p. 98—100°, raised to 101—102° after 3 crystallisations from aqueous alcohol. It was identified as *p*-toluenesulphonanilide by analysis (C, 63·2; H, 5·2; N, 5·6. Calc.: C, 63·1; H, 5·3; N, 5·7%), m. p., and mixed m. p.; yield 85%.

Action of Aqueous Sulphuric Acid on m-*Nitrobenzenesulphon*-tert.-*butylanilide* : *Formation of* m-*Nitrobenzenesulphonanilide.*—15*N*-Sulphuric acid (4 c.c.) and 0·40 g. of the *m*-nitrobenzenesulphonyl derivative were heated together for 35 mins. at 100—120°, then at 120—130° for 20 mins., and thereafter for 3 hours at 130—135°. The dark oil floating on the surface of the acid was taken up in ether after dilution with water. Treatment of the ethereal solution with aqueous alkali and subsequent acidification of the alkaline extract yielded 0·27 g. of *m*-nitrobenzenesulphonanilide, m. p. 121—122°, raised to 122—123° (also mixed m. p.) after crystallisation from alcohol; yield 82%. 0·02 G. of unchanged material was recovered.

Action of Sulphuric Acid on Phenyl-tert.-*butylnitrosoamine.*—When the powdered nitrosoamine is treated with concentrated sulphuric acid, it masses together and assumes a deep brown colour. It gradually dissolves with a slight evolution of gas to give a solution which is only feebly tinted. When it is poured on ice, a brownish solution is obtained, which becomes turbid on shaking and then deposits the crystalline nitrosoamine, m. p. 59—61°, mixed m. p. with phenyl-*tert.*-butylnitrosoamine 60—62°. The aqueous solution gives a slight test for a diazo-compound and contains free nitrous acid.

When the nitrosoamine (0·56 g.) is added to concentrated sulphuric acid (3 c.c.) without any external cooling, the solution becomes warm and green, nitrous fumes being evolved; addition of 3 c.c. of 19*N*-sulphuric acid and warming to 45° for 1 hour produced a deep reddish-brown colour. This solution was poured on ice and extracted several times with ether, and when the extract was shaken with aqueous alkali, the aqueous layer assumed an intense green colour which changed to red on acidification and became green again on adding excess of alkali.

The acid aqueous layer remaining after this ethereal extraction gave a deep red colour when poured into alkaline β-naphthol. The precipitate thus formed was collected, dissolved in ether, and the solution filtered from inorganic matter. Evaporation yielded an azo-compound (0·05 g.).

Many attempts were made to find more satisfactory conditions for the preparation of a diazo-compound from the nitrosoamine, but the yield was always small.

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