305. *Reactions of Unsaturated Compounds. Part IV. Addition of Aniline to Olefins.*

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It has been shown (Hickinbottom, J., 1932, 2400) that when trimethylethylene reacts with aniline hydrochloride or hydrobromide, the olefin attaches itself to the nucleus to yield *p*-amino-*tert.*-amylbenzene. It seemed desirable to examine this reaction in greater detail, particularly as many unsaturated hydrocarbons, such as *cyclo*hexene, styrene, and butadiene, not only react with the nucleus of aniline, but also combine with the amino-group to yield a secondary amine (Hickinbottom, J., 1932, 2646; 1934, 319, 1981).

It is now found that, under suitable conditions, the above reaction yields also γ- and β-anilino-β-methylbutane, (I) and (II), in approximately equal proportion; and a similar result is obtained if in this reaction the aniline hydrohalide is replaced by the cobaltobromide or cobaltochloride. This is of interest, in that it is the first example of the combination of an amino-group with an olefin in which there is a serious divergence from the regularities observed for the addition of halogen hydrides to olefins. The reaction of aniline with other olefins, *viz.*, γ-methyl- and γ-ethyl-Δ^{β}-pentene, (III) and (VI), and tetramethylethylene (IX) and octylene, was also examined. Each yielded a mixture of alkylaniline and nuclear-substituted aniline. The relative yields of primary and secondary amines in

$$\text{(I.)}\quad \mathrm{CMe_2Et{\cdot}NHPh} \qquad\qquad \mathrm{CHMe_2{\cdot}CHMe{\cdot}NHPh}\quad \text{(II.)}$$

$$\underset{\text{(III.)}}{\mathrm{CMeEt{:}CHMe}} \longrightarrow \underset{\text{(IV.)}}{\mathrm{CMeEt_2{\cdot}NHPh}} \text{ and } \underset{\text{(V.)}}{\mathrm{CMeEt_2{\cdot}C_6H_4{\cdot}NH_2}}$$

$$\underset{\text{(VI.)}}{\mathrm{CEt_2{:}CHMe}} \longrightarrow \underset{\text{(VII.)}}{\mathrm{CEt_3{\cdot}NHPh}} \text{ and } \underset{\text{(VIII.)}}{\mathrm{CEt_3{\cdot}C_6H_4{\cdot}NH_2}}$$

$$\underset{\text{(IX.)}}{\mathrm{CMe_2{:}CMe_2}} \longrightarrow \underset{\text{(X.)}}{\mathrm{CHMe_2{\cdot}CMe_2{\cdot}NHPh}} \text{ and } \underset{\text{(XI.)}}{\mathrm{CHMe_2{\cdot}CMe_2{\cdot}C_6H_4{\cdot}NH_2}}$$

the product depended largely on the experimental conditions; the use of a considerable excess of aniline and of a relatively small amount of aniline hydrohalide favours the production of an alkylaniline (compare Table II, p. 1281). The structure of the olefin also has a marked influence on the yield of alkylaniline; *e.g.*, although octylene furnishes *sec.*-octylaniline as the principal product, with only a very small amount of *p*-amino-*sec.*-octylbenzene, yet tetramethylethylene, under similar conditions, yields β-*p*-aminophenyl-βγ-dimethylbutane (XI) with only a very small amount of the corresponding alkylaniline (X).

EXPERIMENTAL.

Reaction of Aniline Salts with Trimethylethylene : Formation of p-*Amino*-tert.-*amylbenzene,* tert.-*Amylaniline, and* β-*Anilino*-γ-*methylbutane.*—Trimethylethylene was prepared from *tert.*-amyl alcohol by slow distillation with a small amount of iodine, and purified by refluxing with sodium and fractionation over sodium; it had b. p. 36—37°.

Mixtures of trimethylethylene with an excess of aniline containing some aniline hydrochloride or hydrobromide were heated in sealed tubes at 230—250° for 5½—25 hours. Precise details of some of these experiments are recorded in Table I.

TABLE I.

Aniline, g.	Aniline salt added, and wt., g.		Amylene, g.	Heating.		Yield, g.		
				Temp.	Duration, hrs.	*p*-Amino-*tert.*-amylbenzene.	Amylaniline.	Diphenylamine.
30	PhNH$_2$,HBr	3	6	230—250°	6·5	3·7	0·57	2·05
30	PhNH$_2$,HBr	1	6	230—250	6	1·8	0·51	0·68
40	PhNH$_2$,HBr	4	7·1	240—260	5·5	3·3	1·84	2·01
100	PhNH$_2$,HBr	6	12	240—260	25	6·85	0·59	not detd.
40	PhNH$_2$,HBr	4	7·1	230—255	6	6·7	1·94	2·24

(i) *Isolation of* p-*amino*-tert.-*amylbenzene.* The contents of each batch of tubes were made alkaline and amine was separated, dried, and fractionated to remove as much as possible of the aniline. The residue was treated with a slight excess of *N*-sulphuric acid (Congo-red paper). The precipitate of sulphate was collected, washed with water, and extracted with ether. The filtrate and ethereal washings were reserved (A). The sparingly soluble sulphate consisted of *p*-amino-*tert.*-amylbenzene sulphate mixed with some aniline sulphate; the former base was purified through its acetyl compound.

(ii) *Isolation of diphenylamine.* The filtrate and ethereal washings (A) were combined, the ethereal layer then separated, and the aqueous layer (B) extracted several times with ether. Evaporation of the dried ethereal extracts yielded crude diphenylamine, which after purification was identified by its m. p. and by conversion into the nitrosoamine (m. p. and mixed m. p.).

(iii) *Isolation of* tert.-*amylaniline* (I) *and of* β-*anilino*-γ-*methylbutane* (II). The aqueous solution (B) contained principally secondary amines with some aniline as sulphates. The former were concentrated by the following process. The aqueous solution was rendered alkaline, the amines separated, and the aniline precipitated as zincichloride (compare Hickinbottom, J., 1930, 993). The crude secondary amines thus obtained were treated in aqueous suspension with acetic anhydride (Hickinbottom, J., 1933, 947) and steam-distilled. The amine collected in the distillate boiled at 112—114°/26 mm. and was a mixture of (I) and (II). Separation was accomplished by treating the mixture in pyridine solution with half the theoretical amount of *p*-toluenesulphonyl chloride, and keeping it over-night; water was then added, and the oil which separated was taken up in ether. The ethereal solution was freed from pyridine and unchanged *tert.*-amylaniline by shaking with several successive amounts of dilute hydrochloric acid; addition of sodium nitrite to the aqueous acid extracts yielded phenyl-*tert.*-amylnitrosoamine, m. p. and mixed m. p. 47—48° (Hickinbottom, J., 1933, 950), and evaporation of the ethereal solution yielded a crystalline residue of the p-*toluenesulphonyl* derivative of β-*anilino*-γ-*methylbutane.* After several crystallisations from alcohol, it was obtained pure as lozenge-shaped plates, m. p. 83—84° (Found : C, 67·8; H, 7·1; N, 4·4. $C_{18}H_{23}O_2NS$ requires C, 68·1; H, 7·3; N, 4·4%). Although the m. p. is very close to that (79—80°) of the same derivative of *iso*-amylaniline, a mixture of the two melts below 70°.

Reaction of Aniline Salts with γ-*Methyl*-Δ^{β}-*pentene : Formation of* p-*Amino*-tert.-*hexylbenzene* (V) *and* tert.-*Hexylaniline* (IV).—The olefin was prepared (*a*) by slow distillation of methyldiethylcarbinol with a small amount of iodine, (*b*) by the action of aniline on γ-iodo-γ-methylpentane. Both methods yielded the same material, which was refluxed over sodium and twice fractionated over the same metal; b. p. 69—71°.

The general procedure for bringing about the reaction with aniline and for isolating the products was similar to that already described. The experimental conditions and the yields of the products are summarised in Table II.

TABLE II.

Aniline, g.	Aniline salt added, and wt., g.		Hexylene, g.	Heating.		Yield, g.		
				Temp.	Duration, hrs.	*p*-Amino-*tert.*-hexylbenzene.	Hexylaniline.	Diphenylamine.
40	$PhNH_2$,HBr	2	5·6	260—280°	5	1·41	0·85	1·98
50	$PhNH_2$,HCl	4	10·5	230—270	5	2·7	1·7	3·07
6	$PhNH_2$,HCl	3	3·5	285—290	3·5	1·02	trace	not detd.
6	$PhNH_2$,HCl	2	3·5	260—270	4·5	0·63	0·07	not detd.
5	$PhNH_2$,HCl	2	3·5	250—260	5	2·1	0·12	not detd.

p-*Amino*-tert.-*hexylbenzene* is a liquid with a pale yellow tint, b. p. 135°/28 mm. (Found : C, 81·8; H, 10·4. $C_{12}H_{19}N$ requires C, 81·3; H, 10·8%). The *hydrochloride* crystallised from warm dilute hydrochloric acid in leaflets (Found : HCl, 17·2. $C_{12}H_{19}N$,HCl requires HCl, 17·1%), fairly easily soluble in water and precipitated from aqueous solution by the addition of hydrochloric acid. The *sulphate* was obtained as white platelets, sparingly soluble in water [Found : H_2SO_4, 21·6. $(C_{12}H_{19}N)_2H_2SO_4$ requires H_2SO_4, 21·7%]. The *acetyl* derivative crystallised from aqueous alcohol as thin leaflets, m. p. 102—103° (Found : C, 76·5; H, 9·3; N, 6·7. $C_{14}H_{21}ON$ requires C, 76·7; H, 9·7; N, 6·4%), and the p-*toluenesulphonyl* derivative formed silky needles, m. p. 119—120°, from the same solvent (Found : C, 69·3; H, 7·8. $C_{19}H_{25}O_2NS$ requires C, 68·8; H, 7·6%).

The *tert.*-hexylaniline, isolated from the reaction product, was purified by treatment with aqueous acetic anhydride, followed by 2 days' contact with a small amount of *p*-toluenesulphonyl chloride. Steam-distillation of the latter mixture after the addition of sodium carbonate yielded pure *tert.*-hexylaniline, b. p. 123—124°/23 mm. (Hickinbottom, J., 1933, 950, gives 120—121°/17 mm.). It was characterised by its *picrate*, a golden-yellow, crystalline mass, m. p. 130—132°, from benzene–light petroleum (Found : C, 52·8; H, 5·4; N, 13·8. $C_{12}H_{19}N,C_6H_3O_7N_3$ requires C, 53·2; H, 5·4; N, 13·8%); a specimen prepared from the base derived from *tert.*-hexyl iodide melted at 132—133° under similar conditions, and a mixture of the two specimens at 131—132°.

Reaction of Aniline Salts with γ-Ethyl-Δ^β-pentene : Formation of p-*Amino*-tert.-*heptylbenzene* (VIII) *and* tert.-*Heptylaniline* (VII).—The olefin was prepared by the slow distillation of triethylcarbinol with a small amount of iodine; another specimen was obtained by the action of aniline on *tert.*-heptyl iodide (p. 1282). Both specimens were identical and were purified by boiling over sodium for several hours; b. p. 96—97° (Saytzeff, *J. pr. Chem.*, 1898, **57**, 39, gives b. p. 97—98°).

Aniline (50 g.), aniline hydrochloride (8 g.), and γ-ethyl-Δ^β-pentene (10 g.) were heated together in sealed tubes for 12 hours at 230—260°. The product was a dark liquid resting on a small amount of crystalline material. It was worked up by a process similar to that described for the reaction with trimethylethylene. After removal of aniline and diphenylamine, the product (1·99 g.) had b. p. 130—145°/18 mm. This furnished 1·22 g. of primary and 0·35 g. of secondary amine. Another preparation, from 30 g. of aniline, 6 g. of the hydrochloride, and 10·9 g. of the olefin (20 hrs. at 230—260°), gave 0·71 g. of primary and 0·16 g. of secondary amine.

The primary amine isolated from the mixture consisted very largely of *p*-amino-*tert.*-heptylbenzene, together with an isomeric amine in quantity too small for purification.

p-*Amino*-tert.-*heptylbenzene* (p-*aminotriethylcarbinylbenzene*) was purified through its *acetyl* derivative, which crystallised from aqueous alcohol in leaflets, m. p. 140—141° (Found : C, 77·2; H, 10·0. $C_{15}H_{23}ON$ requires C, 77·2; H, 9·9%), and was thence obtained as a very pale yellow liquid, b. p. 144—145°/32 mm., which solidified on keeping and then crystallised from light petroleum as a mass of white needles, m. p. 56—58° (Found : C, 82·0; H, 10·9. $C_{13}H_{21}N$ requires C, 81·6; H, 11·1%); *hydrochloride* (Found : HCl, 16·4. $C_{13}H_{21}N$,HCl requires HCl, 16·0%).

The secondary amine from the reaction yielded a nitrosoamine, which eventually crystallised and was identified as phenyl-*tert.*-heptylnitrosoamine by comparison with an authentic specimen.

Preparation of tert.-*Heptylaniline* (*γ-Anilino-γ-ethyl*-n-*pentane*).—A mixture of aniline (70 g.) and *tert.*-heptyl iodide (81 g.) soon became solid, and was then heated for ½ hour to complete the reaction. The γ-ethyl-Δ^β-pentene formed was removed by distillation (yield, 20·35 g.;

calc., 34·8 g.). The residue containing aniline and *tert.*-heptylaniline was rendered alkaline, and the amine taken up in ether, dried, and fractionated to remove as much as possible of the aniline. *tert.*-Heptylaniline was isolated from the residue by treating an aqueous suspension with a slight excess of acetic anhydride, keeping it for 24 hours, adding an excess of sodium carbonate, and steam-distilling the mixture. The amine isolated from the distillate was again treated with aqueous acetic anhydride and steam-distilled. tert.-*Heptylaniline* was thus obtained as a refractive, very pale yellow liquid having an odour somewhat like those of its lower homologues containing tertiary alkyl groups; b. p. 131—132°/26 mm. (Found: C, 81·5; H, 11·3. $C_{13}H_{21}N$ requires C, 81·6; H, 11·1%). The *picrate* separated from benzene as bright yellow, prismatic needles, m. p. 129—130° (Found: C, 53·8; H, 5·7. $C_{13}H_{21}N,C_6H_3O_7N_3$ requires C, 54·3; H, 5·8%); and the *nitrosoamine* crystallised from light petroleum (b. p. 40—60°) as six-sided plates or stout prismatic needles, m. p. 49—50° (Found: C, 71·1; H, 9·5. $C_{13}H_{20}ON_2$ requires C, 70·85; H, 9·15%).

The tert.-*heptyl iodide* required for the above preparation was prepared by saturating triethylcarbinol with dry hydrogen iodide. It was a colourless liquid, b. p. 64—66°/21 mm., which soon became slightly brown (Found: I, 56·0. $C_7H_{15}I$ requires I, 56·15%).

Reaction of Aniline Salts with Octylene: Formation of sec.-*Octylaniline.*—The octylene was prepared by the distillation of *sec.*-octyl alcohol with about 5% of its weight of sulphuric acid, and freed from traces of alcohol by prolonged refluxing with sodium. The purified product boiled steadily at 122°, but it was probably a mixture of Δ^{α}- and Δ^{β}-octenes (Senderens, *Compt. rend.*, 1912, **154**, 778).

A mixture of 12 g. of aniline hydrochloride, 40 g. of aniline, and 7·2 g. of octylene was heated at 210—240° for 24 hours in sealed tubes. The product was treated with a slight excess of dilute hydrochloric acid, and then extracted with ether to remove diphenylamine. The aqueous solution was rendered alkaline, and the liberated amines separated and distilled, 1·87 g. being collected at 147—150°/22 mm. This was separated into a primary amine (0·1 g.), the nature of which will be discussed in a subsequent paper, and *sec.*-octylaniline (1·0 g.), b. p. 148—150°/20 mm. It was characterised by its *p*-toluenesulphonyl derivative, m. p. 58—59°.

In order to establish the identity of this amine, sec.-*octylaniline* was prepared by the interaction of *sec.*-octyl bromide (40 g.) and aniline (55 g.). It was a colourless liquid, b. p. 288—289° (corr.)/751 mm., 150°/20 mm. (yield, 30 g.) (Found: C, 82·1; H, 11·3. $C_{14}H_{23}N$ requires C, 81·9; H, 11·3%). The p-*toluenesulphonyl* derivative, prepared in pyridine solution, separated from alcohol as transparent prisms, m. p. 59°, identical with that isolated as described above (Found: C, 69·7; H, 8·1; N, 4·1. $C_{21}H_{29}O_2NS$ requires C, 70·1; H, 8·1; N, 3·9%).

Reaction of Aniline Salts with Tetramethylethylene: Formation of β-p-*Aminophenyl*-βγ-*dimethylbutane* (XI).—The olefin was prepared by the dehydration of pinacolin alcohol by slow distillation after the addition of a small amount of iodine. The product was resolved into two fractions, the principal one being tetramethylethylene, b. p. 69—71°; the other boiled at 55—61° and was probably α-methyl-α-*iso*propylethylene (compare Zelinsky and Zelikow, *Ber.*, 1901, **34**, 3250).

A mixture of aniline (40 g.), tetramethylethylene (5·6 g.), and aniline hydrochloride (6 g.) was heated in sealed tubes for 25 hours at 235—240°, and the product worked up in the usual manner. The resulting primary amine was isolated through its sparingly soluble sulphate and purified by conversion into its *acetyl* derivative (yield, 1·90 g.), which separated from aqueous alcohol or acetic acid as white platelets, m. p. 118° (Found: C, 77·0; H, 9·5; N, 6·6. $C_{14}H_{21}ON$ requires C, 76·7; H, 9·7; N, 6·4%). Hydrolysis of this compound furnished β-p-*aminophenyl*-βγ-*dimethylbutane*, a very pale yellow oil, b. p. 138—139°/23 mm. (Found: C, 81·1; H, 10·8. $C_{12}H_{19}N$ requires C, 81·3; H, 10·8%); its *hydrochloride* formed stellate groups of thin transparent plates, sparingly soluble in hydrochloric acid (Found: HCl, 16·8. $C_{12}H_{19}N,HCl$ requires HCl, 17·1%).

There was evidence of the formation of a secondary amine in this reaction, for the filtrate from the sulphate of the primary amine (see above) furnished an amine, which, after treatment with aqueous acetic anhydride, followed by steam-distillation, afforded 0·05 g. of an amine (from 12 c.c. of olefin), b. p. *ca.* 125—130°/21 mm., which furnished a nitrosoamine. The amount available was too small for further examination.

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[*Received, July* 18*th*, 1935.]