79. *Reactions of Unsaturated Compounds. Part II. Addition of Arylamines to Styrene.*

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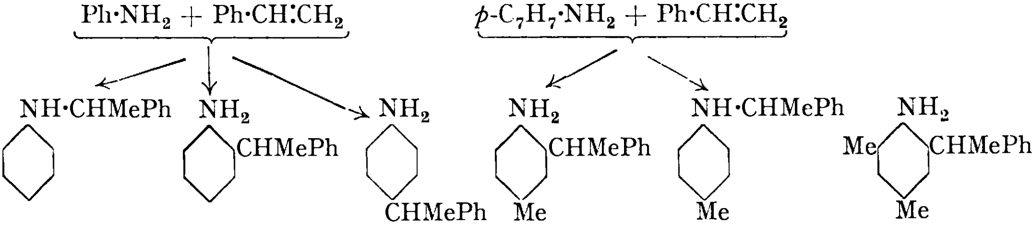
ANILINE, in presence of its hydrochloride or hydrobromide, reacts with styrene at 220—260° to yield α-phenylethylaniline (I) together with relatively larger amounts of *o*- (II) and *p*-α-phenylethylaniline (III) (*o*- and *p*-aminodiphenylethane).

The structure of (III) was determined by replacing the amino-group by bromine by the diazo-reaction, and oxidising the bromo-hydrocarbon to *p*-bromobenzophenone. The application of the same method to determine the structure of (II) was unsatisfactory, for the corresponding bromo-compound could not be oxidised smoothly to a bromobenzophenone. It was possible, however, to establish that both phenyl groups are attached to the same carbon atom by replacing the amino-group by hydrogen and oxidising the resulting hydrocarbon to benzophenone. It was not found practicable to establish directly the orientation of the amino-group, but, in view of the many established cases of *o*- and *p*-substitution in the nucleus of aniline it is extremely unlikely that the amino-group is in any position other than that assigned.

Styrene reacts also with *p*-toluidine in presence of its hydrochloride to furnish a mixture of 3-*α-phenylethyl*-p-*toluidine* (IV) and *α-phenylethyl*-p-*toluidine* (V). The reaction takes place, however, less readily than with aniline. This is still more marked when *m*-4-xylidine reacts with styrene; the yield of (VI) is comparatively small, so it was not examined in any great detail.



(I.) (II.) (III.) (IV.) (V.) (VI.)

The formation of secondary amines in these reactions supplements the only previously recorded examples of the addition of an amino-group at the double bond of an unsaturated hydrocarbon (Hickinbottom, J., 1932, 2646). The best yield of secondary amine was obtained by heating styrene and the amine salt with an excess of the free amine (Table I).

The addition of aniline may take place to yield either α- or β-phenylethylaniline. The structure (I) was proved by the identity of the secondary amine (and its derivatives) with the amine (and its derivatives) prepared by the addition of methylmagnesium iodide to benzylideneaniline (Busch, *Ber.*, 1904, **37**, 2691). The structure of (V) was established similarly.

EXPERIMENTAL.

Addition of Aniline to Styrene.—Styrene, aniline, and a suitable promoter were heated together in a sealed tube at 220—240° for 6 hours. After cooling, the black semi-solid product was extracted in succession with ether, water, and dilute hydrochloric acid. A moderate excess of 3*N*-hydrochloric acid was added to the combined extracts; the ethereal layer, after being shaken with several separate quantities of 3*N*-hydrochloric acid, contained chiefly styrene, polymerised styrene, and some diphenylamine. The aqueous acid extracts were combined and treated with aqueous ammonia, and the liberated amines were dissolved in ether, dried, and distilled to remove as much aniline as possible. The residue (A) contained *o*- and *p*-α-phenylethylaniline and a smaller amount of α-phenylethylaniline. The following table shows the yields obtained in several preparations after 6 hours' heating.

Aniline, g.	Styrene, g.	Promoter.		Temp.	Yield,		
					o-amine, g.	*p*-amine, g.	*sec.*-amine, g.
5	5	$PhNH_2,HCl$	2 g.	270°	1·75	1·75	trace
14	9	$CdCl_2$	12 g.	200—255	0·93	1·15	—
40	10·8	$PhNH_2,HCl$	8 g.	200—240	1·56	3·70	0·68

(i) *Isolation of* p-*α-phenylethylaniline* (III). The mixture of amines (A) was treated with *N*-sulphuric acid till the resulting paste, after vigorous stirring, was slightly acid to Congo-paper. After 12 hours, the sulphate was collected and washed with ether; the filtrate (B) was reserved for subsequent treatment. The sparingly soluble sulphate was treated with an excess of aqueous ammonia and the liberated amine was dissolved in benzene, washed, dried, and precipitated as picrate by a hot concentrated solution of picric acid in benzene (filtrate C). The picrate was decomposed with aqueous ammonia, and the liberated amine converted into p-α-*phenylethylacetanilide*, which separated from aqueous alcohol in platelets, m. p. 112—113° (Found : C, 80·7; H, 7·2; N, 6·0; *M*, Rast, 263. $C_{16}H_{17}ON$ requires C, 80·3; H, 7·2; N, 5·9%; *M*, 239). This was hydrolysed with 20% hydrochloric acid, and subsequent treatment with excess of sodium hydroxide solution yielded *p*-α-phenylethylaniline as a pale yellow oil, b. p. 176—178°/20 mm. (Found : C, 85·3; H, 8·0. Calc. for $C_{14}H_{15}N$: C, 85·2; H, 7·7%).

The *hydrochloride* separated from dilute hydrochloric acid in transparent lath-like crystals, usually grouped in bundles (Found : HCl, 15·6. $C_{14}H_{15}N,HCl$ requires HCl, 15·6%). The *picrate* formed nodular aggregates of bright yellow, slender needles, m. p. 197—199° (decomp.), from alcohol–benzene (Found : N, 13·2. $C_{14}H_{15}N,C_6H_3O_7N_3$ requires N, 13·1%), sparingly soluble in benzene, not easily in ether, moderately easily in cold alcohol and more readily in the warm solvent. The benzoyl derivative separated from alcohol in thin elongated plates, m. p. 127—128° (Found : N, 4·5. Calc. : N, 4·6%) (Busch and Rinck, *Ber.*, 1905, **38**, 1763, give m. p. 123°). The *m*-nitrobenzenesulphonyl derivative formed a felted mass of slender needles from aqueous alcohol, m. p. 122—123° after softening at 120°. Diazotisation of the amine in an excess of 5*N*-sulphuric acid, followed by distillation in steam, yielded *p*-hydroxydiphenylethane in white needles, m. p. 56—57° (Koenigs and Carl, *Ber.*, 1891, **24**, 3894, record m. p. 57—58°).

Preparation of p-*bromobenzophenone from* p-α-*phenylethylaniline.* The amine was diazotised in an excess of dilute hydrobromic acid and treated with concentrated hydrobromic acid and copper-bronze. After several hours the *p*-bromodiphenylethane was distilled in steam, dissolved in ether, washed with dilute aqueous sodium hydroxide, recovered, and gradually treated (0·3 g. in 5 c.c. of glacial acetic acid) with 0·6 g. of chromium trioxide in the minimum amount of 50% acetic acid. The solution was boiled under reflux for 20 minutes, the excess of chromic acid destroyed by addition of dilute sulphuric acid and sodium bisulphite, and the solution diluted considerably with water and extracted several times with ether. Evaporation of the ethereal extract, after being washed with dilute aqueous alkali and dried, left an oil which rapidly solidified, m. p. 76—79° after draining on porous earthenware (yield, 0·12 g.), raised by crystallisation from aqueous alcohol to 80—81°, which was not altered by admixture with authentic *p*-bromobenzophenone.

(ii) *Isolation of* o-α-*phenylethylaniline* (II). The filtrates (B) and (C) (pp. 320, 321) were treated with an excess of aqueous ammonia, and the amines taken up in benzene. The benzene solution was washed, dried, and evaporated, and the residue extracted repeatedly with hot, very dilute hydrochloric acid. The combined acid extracts were made alkaline with ammonia, and the liberated amines were taken up in ether, washed with water, and mixed with a moderate excess of fairly concentrated hydrochloric acid. The hydrochloride of o-α-*phenylethylaniline* separated as a crystalline paste. The filtrate (D) was reserved for further treatment. The free amine separated from light petroleum (b. p. 40—60°) as a mass of acicular crystals, m. p. 58—59° (Found : C, 85·5; H, 7·9; N, 7·3; *M*, Rast, 205. $C_{14}H_{15}N$ requires C, 85·2; H, 7·7; N, 7·1%; *M*, 197), easily soluble in the more common solvents except light petroleum.

The *hydrochloride* separated from dilute hydrochloric acid as clusters of very thin, transparent plates (Found : HCl, 15·6. $C_{14}H_{15}N,HCl$ requires HCl, 15·6%). The *acetyl* derivative formed small compact crystals from ethyl alcohol, m. p. 112—113° (Found : C, 80·7; H, 7·3; N, 5·8. $C_{16}H_{17}ON$ requires C, 80·3; N, 7·2; N, 5·9%); mixed with the *p*-compound, it melted at 90—94°. The *benzoyl* derivative formed colourless needles, m. p. 95—96°, from benzene–light petroleum (Found : C, 84·0; H, 6·5; N, 4·8. $C_{21}H_{19}ON$ requires C, 83·7; H, 6·4; N, 4·6%), fairly readily soluble in benzene, alcohol, or ether, but less soluble in light petroleum.

Preparation of benzophenone from o-α-*phenylethylaniline.* A solution of the amine (0·55 g.) in 10 c.c. of 5*N*-hydrochloric acid was diazotised, filtered, mixed with 20% aqueous sodium hydroxide at 0°, and added to alkaline stannite. A reddish oil separated, which after 2 days was taken up in ether, washed with aqueous alkali and acid, and steam-distilled. The hydrocarbon extracted from the distillate by ether was a colourless liquid with a pleasant odour (0·33 g.). It was oxidised by acetic acid–chromium trioxide (2 g.) as described above, the diluted solution treated with alcohol to reduce the excess of chromium trioxide, and the product extracted in ether, washed (sodium carbonate solution and aqueous alkali), dried, and recovered as an oil (0·23 g.), which, after solidification and crystallisation from alcohol, had m. p. 47—48°, alone or mixed with authentic benzophenone (phenylhydrazone, m. p. and mixed m. p. 136—137°).

(iii) *Isolation of α-phenylethylaniline* (I). The filtrate (D) (p. 321) was treated with alkali, and the liberated amine taken up in ether and shaken several times with 3N-hydrochloric acid. The combined acid extracts were made alkaline and the amine, which separated, was distilled under reduced pressure after the usual treatment. The main fraction, b. p. 158—170°/23 mm., was a pale yellow, viscous oil which furnished a sparingly soluble nitrate, m. p. 158—160° (decomp.), on treatment with 3N-nitric acid. The amine liberated from the nitrate gave a nitrosoamine and was characterised by its *p*-toluenesulphonyl derivative, m. p. 95—96°.

For comparison, α-phenylethylaniline was prepared by Busch's method (*loc. cit.*) : it had b. p. 171—172°/21 mm. and formed a sparingly soluble nitrate, m. p. 160—161° (decomp.), and a p-*toluenesulphonyl* derivative, white needles from alcohol, m. p. and mixed m. p. 95—96° (Found : C, 72·2; H, 6·2. $C_{21}H_{21}O_2NS$ requires C, 71·8; H, 6·0%).

Addition of p-*Toluidine to Styrene*.—Styrene (10 g.), *p*-toluidine (40 g.), and *p*-toluidine hydrochloride (8 g.) were heated together in sealed tubes to 260° during 2½ hours and then at 260—270° for 5½ hours. The cold product, a crystalline mass, was treated as in the experiment with aniline (pp. 320, 321).

(i) *Isolation of* 3-α-*phenylethyl*-p-*toluidine* (IV). The residue corresponding to (A), on treatment with warm N-sulphuric acid, gave a crystalline sulphate, which was recrystallised from very dilute sulphuric acid (the filtrates from these separations were reserved; B′) and reconverted into the amine (2·9 g.), the *acetyl* derivative of which, crystallised from alcohol, had m. p. 141—142° (Found : C, 80·2; H, 7·5; N, 5·4. $C_{17}H_{19}ON$ requires C, 80·6; H, 7·6; N, 5·5%) and on hydrolysis with boiling 20% hydrochloric acid, followed by steam-distillation of the basified solution, yielded 3-α-*phenylethyl*-p-*toluidine* as a very pale yellow, viscous oil, b. p. 173—174°/18 mm. (Found : C, 85·3; H, 8·1. $C_{15}H_{17}N$ requires C, 85·3; H, 8·1%).

From the respective dilute acid solutions, the *hydrochloride* separated as four-sided tablets (Found : HCl, 14·6. $C_{15}H_{17}N,HCl$ requires HCl, 14·7%), the *hydrobromide* as aggregates of stout prismatic crystals (Found : HBr, 27·5. $C_{15}H_{17}N,HBr$ requires HBr, 27·7%), and the *sulphate* as an asbestos-like mass of crystals, sparingly soluble in cold water [Found: H_2SO_4, 19·1. $(C_{15}H_{17}N)_2,H_2SO_4$ requires H_2SO_4, 18·9%]. The *picrate* crystallised from benzene as bright yellow, nodular aggregates of small needles, m. p. 162—163° (Found : C, 56·8; H, 4·8. $C_{15}H_{17}N,C_6H_3O_7N_3$ requires C, 57·3; H, 4·6%), not readily soluble in cold benzene, but readily in acetone, and the p-*toluenesulphonyl* derivative from alcohol as stellate clusters of prismatic needles, m. p. 122—123° (Found: C, 72·5; H, 6·6. $C_{22}H_{23}O_2NS$ requires C, 72·3; H, 6·4%).

(ii) *Isolation of α-phenylethyl*-p-*toluidine* (V). The filtrates (B′) were made alkaline and the amines liberated were taken up in ether and distilled under reduced pressure, giving first some *p*-toluidine and then a main fraction (0·65 g.) at 165—190°/23 mm., chiefly at 180—184°, which gradually deposited prismatic crystals, m. p. 69—70° after recrystallisation from methyl alcohol. This amine yielded an oily nitrosoamine, was characterised as its *p*-toluenesulphonyl derivative, m. p. 86—87°, and was identified as *α-phenylethyl*-p-*toluidine* by comparison with the specimen prepared as described below.

Preparation of α-phenylethyl-p-*toluidine from benzylidene*-p-*toluidine*. Freshly distilled benzylidene-*p*-toluidine (45 g.) in dry ether was added to an ethereal solution of methylmagnesium iodide prepared from 33 g. of methyl iodide. When the reaction had moderated, the mixture was heated under reflux for 2 hours. As much as possible of the ether was then distilled off slowly, and the residue treated with ice and ammonium chloride. The oil which separated was taken up in ether and extracted with dilute hydrochloric acid. From the acid extracts, made alkaline, the secondary amine separated as an oil, which solidified and then crystallised from light petroleum in massive prisms, m. p. and mixed m. p. 69—70°, b. p. 183—184°/23 mm. (Found : C, 85·1; H, 8·1. $C_{15}H_{17}N$ requires C, 85·3; H, 8·1%), not readily soluble in cold light petroleum or cold ethyl alcohol.

The p-*toluenesulphonyl* derivative, prepared by means of *p*-toluenesulphonyl chloride in pyridine, crystallised from methyl alcohol as aggregates of short slender needles, m. p. 86—87° (Found : C, 72·3; H, 6·2. $C_{22}H_{23}O_2NS$ requires C, 72·3; H, 6·4%).

Addition of m-4-*Xylidine to Styrene*.—A mixture of *m*-4-xylidine hydrochloride (4 g.), *m*-xylidine (5 g.), and styrene (4·5 g.) was heated in a sealed tube for 4 hours at 255—290° after a preliminary heating of 4 hours. The soft crystalline product, worked up by a process similar to those employed in the previously described additions, gave 3 g. of polymerised styrene and a mixture of amines which still contained a considerable amount of *m*-xylidine. This mixture was diluted with benzene and treated with picric acid; a precipitate of *m*-xylidine picrate was obtained. The more soluble fractions were treated with an excess of aqueous ammonia, and the liberated amines acetylated. By fractional crystallisation the *acetyl* derivative of 5-α-phenylethyl-*m*-4-xylidine (VI) was obtained pure (0·4 g.); it separated from alcohol in small rosettes, m. p. 148—149° (Found: C, 80·7; H, 7·6; N, 5·5. $C_{18}H_{21}ON$ requires C, 80·85; H, 7·9; N, 5·2%).

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